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PRESSURE-TEMPERATURE DIAGRAMS FOR BINARY SYSTEMS

BY WILDER D. BANCROFT

The first complete pressure-temperature diagram was given about a year ago by van't Hoff;[1] but he did not put in the curves for the partial pressures. The object of this paper is to fill this gap in our knowledge to a certain extent, qualitatively. We will first consider systems in which there can be only one liquid phase and in which the only solid phases possible are the two pure components. Two classes are then to be distinguished. In the first the vapor-pressure boundary curves for the less fusible component lie wholly below the corresponding set of curves for the more fusible substance; in the second, the vapor-pressure boundary curves for the less fusible substance lie wholly above the corresponding set of curves for the more fusible component. Intermediate systems with intersecting pressure curves are quite conceivable but do not need be considered in detail.

In Fig. 1 OB is the sublimation curve, OA is the vaporization curve and O the triple point for the more fusible component. O_1B_1 and O_1A_1 are the corresponding curves for the other component, O_1 being the triple point. If the eutectic temperature be that of the points H and H_1, the partial pressure of the more fusible component, while it is solid phase, will be represented by OH provided we ignore any solvent action of the vapors. In the same way the partial pressure of the second component when present as solid phase will be O_1H_1. The partial pressures of the substance which is not present as solid phase are given by D_1H_1 and DH, the curve D_1H_1 belonging with OH while DH goes with O_1H_1. By adding OH and D_1H_1 we get the curve OC, representing the boundary curve for solid, liquid and vapor

[1] Vorlesungen über theoretische Chemie, 35.

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when the more fusible component is solid phase. By adding O_1H_1 and DH we get the curve O_1C, the boundary curve for solid, liquid and vapor when the less fusible component is solid phase. By adding HB and H_1B_1 we get the curve CK, the boundary curve for the two solid components and vapor. The curve for two solids and solution is omitted, so as not to complicate the diagram unnecessarily. It would, of course, run almost vertically from C. Although the pressure corresponding to the

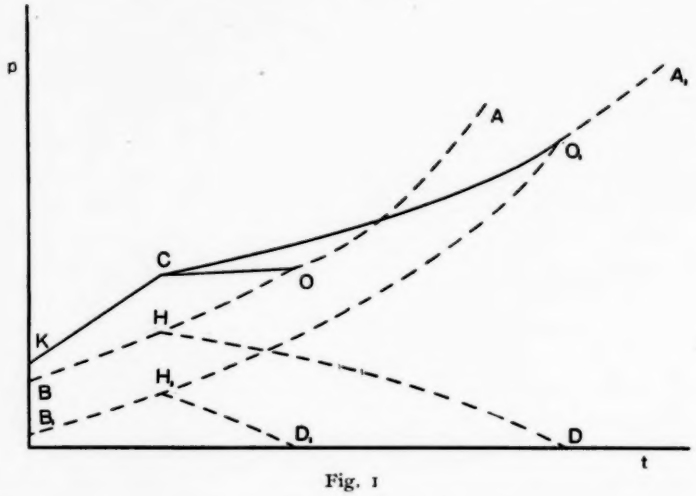


Fig. 1

point C is less than that of the point O in the diagram, it is to be noticed that this is not necessarily the case. If the curves OH and O_1H_1 were to coincide more closely than they do in Fig. 1, the point C would lie above instead of below O. The curves DH and D_1H_1 have been drawn very nearly as though they were straight lines for the excellent reason that little is known about them. When the vapor-pressure of the less fusible component at the triple point is very much lower than the vapor-pressure of the point on OA for the same temperature, we shall have a state of things represented schematically in Fig. 2.

The letters have the same signification as before. The curve DH has a distinctly marked maximum and, in consequence, the curve O_1C passes through a maximum. We know that this must be the case with potassium nitrate and water because a

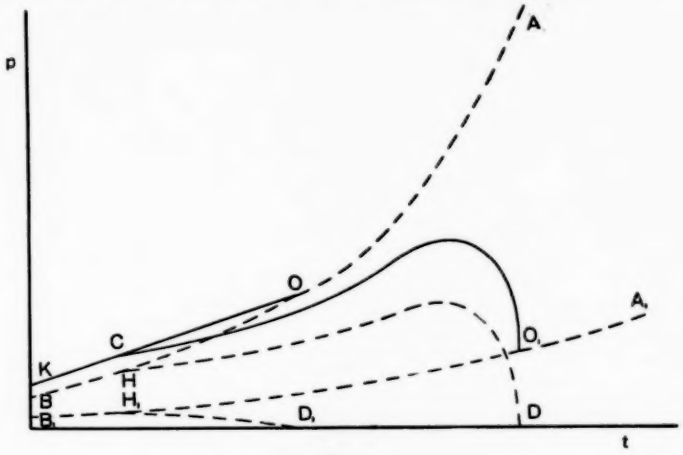


Fig. 2

solution saturated with respect to the salt boils under atmospheric pressure at about 120° while the vapor-pressure of potassium nitrate at its melting-point is scarcely measurable. This is the case cited by van't Hoff; but the phenomenon is very general. For instance, Stortenbeker[1] found that when the freezing-point of iodin was lowered by the addition of chlorin, the vapor-pressure of the system first increased and then decreased.

In Fig. 3 is given the general diagram for the case in which the vapor-pressure curves for the less fusible component lie wholly above the corresponding set of curves for the other substance. The letters have the same signification as before. In a system coming under this head, the pressure corresponding to the point C will usually be higher than that of the point O;

[1] Zeit. phys. Chem. **3**, 19 (1889).

but this is not necessarily the case. It is conceivable that if the temperature and pressure of O differed but little from that of O_1 and if the temperature of C were sufficiently low, the pressure corresponding to the point O might be higher than that of C. It seems probable that this will be the exceptional case, though it

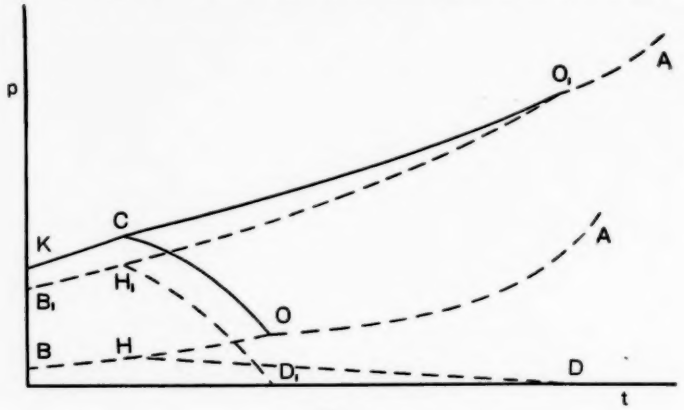


Fig. 3

is the more probable state of things when there are intersecting vapor-pressure curves.

A very interesting case occurs when the less fusible component is more dense as solid than as liquid and when the other component is a gas at the temperature of O_1. If we assume that the gas is practically insoluble in the liquid formed by melting the less fusible component, the pressure of the gas will be a more important factor than its solubility and we shall have a rise of freezing-point. This brings up the partial pressure of the solvent in the vapor phase. Ordinarily we say that the solid solvent is in equilibrium with solution and vapor when the partial pressure of the solvent in the system, solution and vapor, is equal to the vapor-pressure of the solvent in the system, solid and vapor. If we exclude a possible solvent action of the gas, this definition seems to be a sound one, and it follows therefore that the partial pressure of the solvent in the system, solid sol-

vent, solution and vapor, will be equal, at temperatures above the melting-point, to the vapor-pressure of the system, superheated solid and vapor. The details of such a system are shown in Fig. 4, with a complete disregard of scale. The apparent minimum in O_1A_1 is not to be taken seriously. It owes its existence to a desire not to crowd the curve O_1O_2.

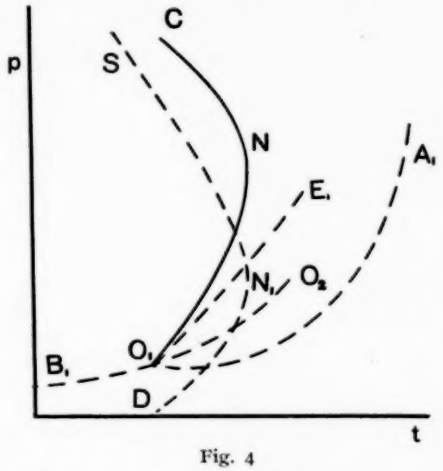


Fig. 4

O_1A_1, O_1B_1 and O_1E_1 are the boundary curves for pure liquid and vapor, solid and vapor, solid and liquid respectively. O_1O_2 is the prolongation of B_1O_1, the system being instable with respect to the liquid phase. The partial pressure of the gas is given by the curve DS. This, of course, continues to the next quadruple point; but we shall only consider the curves in the immediate neighborhood of the point O_1 so that it is quite immaterial whether the new phase appearing at the next quadruple point be pure solid, a compound or a second solution. The total vapor-pressure of the system is represented by O_1NC. If the gas were absolutely insoluble in the melt, this curve would coincide with O_1E_1. As this can never be the case theoretically, the curve O_1NC will always lie above O_1E_1. In the construction of Fig. 4 it has been assumed that with increasing pressure

the gas becomes more and more soluble in the melt until, at length, the lowering of the freezing-point due to the solubility overbalances the rise of freezing-point due to the increase of pressure. It has recently been pointed out by Tammann[1] that systems of this sort have been studied by Danien,[2] the components being air and naphthylamin, diphenylamin, paratoluidin or mononitronaphthalene. In Fig. 4 the temperature and pressure of the maximum freezing-point are represented by the point N. The point N_1 denotes the point on the curve O_1O_2 at which the temperature is that of the maximum freezing-point. As the total pressure of the system increases from O to N, the partial pressure of the less fusible component increases from O_1 to N_1. As the total pressure of the system changes from N to C, the partial pressure of the solvent decreases from N_1 back to O_1 and is represented by the curve O_1B_1 as the system passes along the prolongation of O_1NC.

Since the field for solution and vapor is bounded by A_1O_1 and O_1NC, it is obvious that if we start at some point on O_1A_1 having a temperature lower than that of the point N and add the gas continuously at constant temperature keeping the volume of the system constant, the pressure will change until the solid phase appears at the pressure represented by the point on O_1N for that temperature. During this process the partial pressure of the solvent has increased from that of a point on O_1A_1 to a pressure represented by a point on O_1O_2. From this we see that if we compress a liquid by means of a gas practically insoluble in it, we shall increase the partial pressure of the liquid quite apart from any solvent action of the gas. This phenomenon has been observed by Schiller[3] and has been discussed at some length by Ostwald.[4] From the diagram we see that, if the gas exerts no solvent action, the curve O_1O_2 represents the limiting partial pressures that can be reached in this way. In the same way in-

[1] Wied. Ann. **66**, 477 (1898).
[2] Comptes rendus, **112**, 785 (1891).
[3] Wied. Ann. **60**, 755 (1897).
[4] Lehrbuch, **2**, II, 361.

crease of pressure at temperatures below that of O_1 will cause an increase in the partial pressure of the less fusible component, the limiting values given by the prolongation of A_1O_1.

Up to this point we have expressly excluded any solvent action in the vapor phase; but it is now desirable to determine what will be the effect of dropping this limitation. In Fig. 5 is

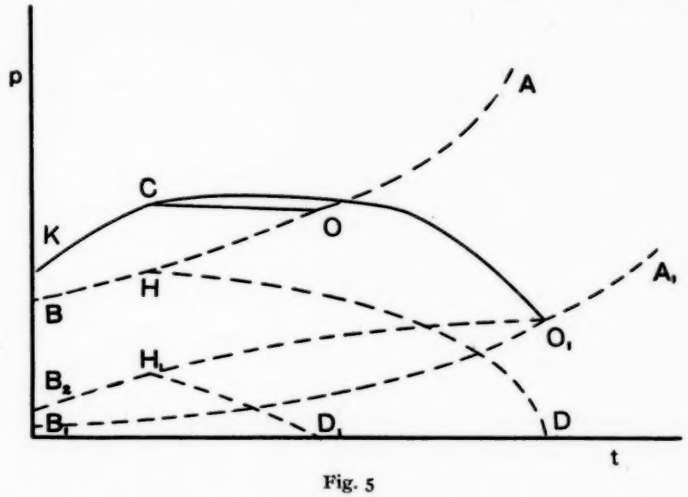


Fig. 5

given the diagram for a system in which such a solvent action takes place. To avoid cumbering the diagram with unnecessary curves, the assumption has been made that the vapor of the less fusible component exercises no perceptible solvent action on the other substance. The effect of this limitation will be pointed out in the discussion.

The essential feature of this system, in which it differs from that shown in Fig. 2, is the presence of the curve $O_1H_1B_2$. The partial pressure of the less fusible component when present as solid phase cannot be represented by the curve O_1B_1; as heretofore because that is the state of things when the solvent action of the vapor is excluded. The curve $O_1H_1B_2$ represents the partial pressures of the less fusible component when it is present as

solid phase in equilibrium with solution and vapor. It should be understood that no attempt has been made to draw any of these diagrams to scale. When some actual system coming under this head is studied, it will probably be found that $O_1H_1B_2$ passes through a maximum very near the point O_1 and that, for the rest of its course, it will coincide very nearly with O_1B_1. In the same way it is more than probable that, in all cases in which the divergence of $O_1H_1B_2$ from O_1B_1 is marked, the curve DH will pass through a maximum just as in Fig. 2. These, however, are matters of detail varying from one system to another and have no effect on the general relations. If we were to take into account a solvent action due to the vapor of the less fusible component we should have a curve starting from O and lying just above OB. The point H would then be on this new curve and not on OB. If there were a point of maximum temperature on the curve O_1C we should also have to consider a curve starting from O_1 and lying above the prolongation of B_1O_1.

From the last diagram it was clear that, when one component can dissolve in the vapor of the other, the partial pressures for the solvent in the system, solid solvent, solution and vapor, are given by a curve starting from the triple point and lying above the boundary curve for solid and vapor. The reverse state of things will be found in case the solid phase has a perceptible solvent action; in other words, in case a solid solution is formed. In Fig. 6 is given the diagram for a system in which two systems of solid solutions are possible.

OA is the vaporization curve and OB the sublimation curve for one of the pure components; O_1A_1 and O_1B_1 the corresponding curves for the other pure component. OHL gives the partial pressures of the more fusible component in one set of saturated solid solutions at different temperatures, while O_1H_1 gives the relation between the temperature and the partial pressure of the less fusible component when the solid phase is the other set of saturated solid solutions. If the temperature of the eutectic point be that of the points C, H and H_1, the partial pressures of the solutes along the two boundary curves may be represented

by D_1H_1 and DH respectively. The boundary curves for the system are $OC = OH + D_1H_1$, $O_1C = O_1H_1 + DH$, and $CK = HL + H_1L_1$.

In cases where no solid solutions are possible the curve OC must lie above the curve OB because it is equal to the curve OB plus the curve for the partial pressures of the other component. When solid solutions occur, this is no longer necessary and in the present rather extreme case the curve OC lies completely below OB.

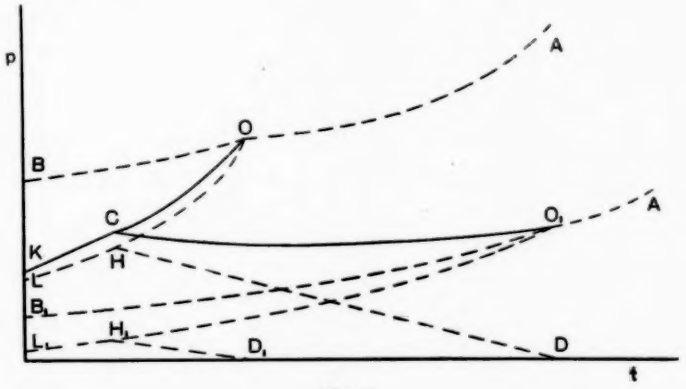


Fig. 6

If the two substances form one continuous series of solid solutions, the curves HL and H_1L_1 disappear and we have two continuous curves OHD and $O_1H_1D_1$. For the isomorphous mixtures studied by Küster[1] OHD and $O_1H_1D_1$ become the straight lines OD and O_1D_1, and we have a state of things represented graphically in Fig. 7.

OD gives the partial pressures for the more fusible component in the system, solid solution, liquid solution and vapor, while O_1D_1 gives the corresponding values for the other. The sum of these two curves is OO_1, which represents the total vapor-pressure along the boundary curve. Of course, it is very im-

[1] Zeit. phys. Chem. **8**, 577 (1891).

probable that the curves OD and O_1D_1 are ever absolutely straight lines, but this diagram may be considered as the limiting case.

There is one other point that calls for discussion. At temperatures below that of the quadruple point, hydrated sodium

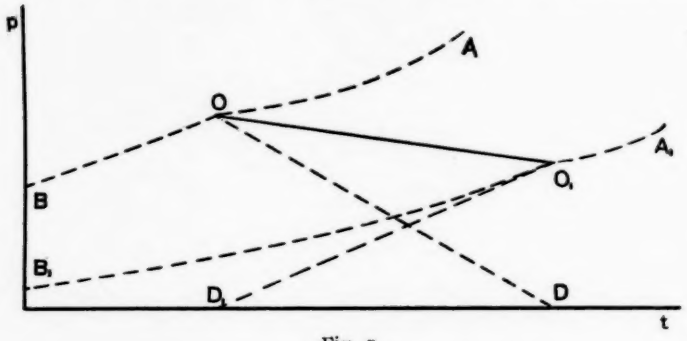


Fig. 7

sulfate can exist in stable equilibrium with solution and vapor, while the system, anhydrous sodium sulfate, solution and vapor, though realizable experimentally, is instable with respect to the hydrated salt. The metastable solution contains more sodium sulfate than the other and has a lower vapor-pressure. In one-component systems the phase that is in equilibrium with vapor at a higher pressure is instable with respect to the phase that is in equilibrium with vapor at a lower pressure. At first sight it would appear as though the solution saturated with respect to the anhydrous salt should be the more stable or, at any rate, that the difference of vapor-pressures would tend to change the equilibrium in one direction and that the difference of concentrations would tend to displace the equilibrium in the opposite direction, the latter tendency being the decisive one. As a matter of fact there is no such conflict of forces. Let the solution saturated with respect to the hydrated salt be called A and the solution saturated with respect to the anhydrous salt be called B. If these two solutions are brought in contact, salt will diffuse

from the place of higher concentration to that of lower concentration, in other words from B to A. The solution A being saturated, by definition, the salt that has diffused in will crystallize as decahydrate; in the meanwhile salt will dissolve in B to restore the original concentration and will then diffuse into A. The final result will be the disappearance of the anhydrous salt and of the difference between the solutions. The actual result, apart from the question of transference, will be that anhydrous salt goes into solution and that hydrated salt crystallizes.

Suppose, now, that the solutions be so arranged that they have a common vapor phase, diffusion however being impossible. This may be done by placing the solutions in two beakers under a bell-glass. Water will then distil from the place of higher pressure to the place of lower pressure, in other words from A to B. The solution in A will tend to become more concentrated and hydrated salt will therefore separate. The solution in B will tend to become more dilute and equilibrium will continually be restored by the anhydrous salt going into solution. The final equilibrium will depend on the relative masses of the phases. If the mass of solution in A be relatively small with reference to the mass of solution or to the mass of anhydrous salt in B, the final equilibrium will be hydrated crystals in A, solution and anhydrous salt in B. If the mass of solution be not relatively small with reference to either of the phases in B, the final equilibrium will be hydrated crystals and solution in A and a solution of the same composition in B. Whatever be the final combination of phases, the change taking place has been that anhydrous salt goes into solution and hydrated salt crystallizes. We see, therefore, that the anhydrous salt is the metastable form whether we consider the matter from the point of view of the vapor-pressures or of the concentrations.

Cornell University

THE DISSOCIATIVE POWER OF SOLVENTS

BY LOUIS KAHLENBERG AND AZARIAH T. LINCOLN

The theory of electrolytic dissociation has greatly stimulated inquiry into the electrical conductivity of solutions. Naturally aqueous solutions, which possess the power of conducting electricity in a high degree, have thus far attracted most attention. Solutions in which the solvents are mixtures of water and other liquids, especially alcohols, have been studied, and lastly attention has been turned to the investigation of the conductivity of solutions that contain no water.[1] The investigation of the electrical conductivity of this latter class of solutions is of great interest in answering the question as to the cause of the dissociative power of solvents. It need scarcely be stated that the use of non-aqueous solutions as electrolytes would prove of considerable industrial value.

Nernst has pointed out that the greater the dielectric constant of a solvent is, the greater is its dissociative power. Proportionality between the two, however, does not exist. Dutoit and Aston[2] claim that only those solvents that in the liquid state are to be regarded as polymerized possess dissociative power. They show that compounds that contain no oxygen, such as nitriles, when used as solvents, yield solutions that conduct electricity very well. Brühl[3] claims that solvents possessing dissociative power contain elements that have unsatisfied valences or, in other words, are unsaturated compounds. He

[1] H. P. Cady, Jour. Phys. Chem. **1**, 707 (1897). E. Bouty, Comptes rendus, **106**, 595 (1888). Dutoit and Aston, Comptes rendus, **125**, 240 (1897). Dutoit and Friedrich, Bull. Soc. Chim. Paris, (3) **19**, 321 (1898). St. v. Laszczynski u. St. v. Gorski, Zeit. Elektrochemie, **4**, 290 (1897). C. Carrara, Gazz. chim. Ital. **27**, 1, 207 (1897). See also Jahrbuch f. Elektrochemie, **1897**, 45.

[2] l. c.

[3] Zeit. phys. Chem. **18**, 514 (1895); Ibid **27**, 317 (1898); Ber. chem. Ges. Berlin, **30**, 163 (1897).

ascribes the polymerization of the molecules of the solvent as well as the dissociative power that the latter exerts upon the dissolved substance to these spare valences. His theory of the tetravalency of oxygen is used to explain the dissociative power possessed by so many oxygen compounds. That some compounds containing nitrogen, when used as solvents, yield solutions that conduct electricity, Brühl explains is due to the fact that in these compounds nitrogen is a triad and that the dissociative power of the solvent is due to the extra valences of the element. He predicts that hydrazine will prove to have dissociative power; and that in general, in the case of nitrogen compounds this property will vary with the nitrogen content (without being proportional to it, however) just as he claims it varies with the oxygen content in oxygen compounds. He also predicts that all amines will prove to have dissociative power, which will be found to increase with the activity of the compounds. Finally diazo compounds, anhydrous hydrocyanic acid, and even unsaturated compounds of elements other than nitrogen, viz.: — the trichlorides of phosphorus and arsenic, mercaptans and sulphur ethers will according to Brühl be found to have dissociative power. The theory of Brühl will be considered again after the experimental data have been presented, as will also the theories of Nernst and of Dutoit and Aston.

We have for some time been working on the problem of the electrical conductivity of solutions that are not aqueous. In connection with the conductivity determinations we have in a few cases ascertained the molecular weights of the dissolved substances by either the boiling- or freezing-point methods. Since the promulgation of the theory of electrolytic dissociation by Arrhenius[1] it has been assumed that whenever any solution conducts electricity the dissolved substance in it is dissociated electrolytically and consequently the solvent possesses dissociative power. In using the term dissociative power as we do in this paper this assumption has been retained. In view of the splendid success achieved by the theory of electrolytic dissociation in

[1] Zeit. phys. Chem. 1, 631 (1887).

explaining the various properties of aqueous solutions of salts, acids and bases, one would be disposed to apply the same to non-aqueous solutions without further question. It is pertinent to inquire, however, whether in non-aqueous solutions that conduct electricity the dissolved substances are in the dissociated condition; in other words, whether the osmotic pressure, the lowering of the freezing-point or elevation of the boiling-point of the solutions indicates that the molecular weights of the dissolved substances are less than the theoretical to a degree sufficient to account for the conductivity of the solutions. In view of the opposition that the theory of electrolytic dissociation had to meet at the time of its promulgation, and in view of the fact that even at present a number of scientists are opposed to it, we may well hesitate to apply this theory (which is based primarily upon a study of aqueous solutions) to non-aqueous solutions without a firm experimental basis for doing so. In investigating the dissociation power of solvents then, it is very desirable that in connection with conductivity measurements molecular weight determinations be made also, until sufficient data have been collected to establish the fact that in non-aqueous as in aqueous solutions dissociation and electrical conductivity go together. It will no doubt be difficult in many cases to draw conclusions from molecular weight determinations, for some of the solutions conduct so poorly that the dissociation cannot be detected, much less estimated by boiling-point or cryoscopic methods. When the solutions conduct sufficiently well, however, this difficulty will not be met.

The conductivity determinations that we have to present are in part qualitative and in part quantitative. In our search for solvents that yield conducting solutions several difficulties were met, the solvent and the dissolved substance had to be perfectly anhydrous, and again the latter had to be sufficiently soluble to allow measurements to be made readily. Thus far the determinations of electrical conductivity in non-aqueous solutions made by others have been largely confined to salts of the alkalies, ammonium and substituted ammonium. The solubility of

these salts we found to be very slight in some of the solvents we desired to test.

It was found that several chlorides of the heavy metals are readily soluble in many solvents; and as these chlorides are not very difficult to prepare in pure anhydrous form, and as on account of the strong ionizing tendency of chlorine in aqueous solutions they suggested themselves as promising objects to try, they were employed as the dissolved substances in our work thus far. The chlorides used are those of the following formulae: — $FeCl_3$, $AlCl_3$, $SbCl_3$, $BiCl_3$, $CuCl_2$, $AsCl_3$, and PCl_3; the last two were used both as solvents and as dissolved substances.

In the majority of cases ferric chloride was found to be the most soluble of these salts, although antimony trichloride was exceedingly soluble in many of the solvents. Cupric and stannous chlorides were found to be sparingly soluble, speaking generally; aluminum chloride reacted with the solvent in many cases liberating hydrochloric acid. Mercuric chloride was generally found to be more soluble than bismuth chloride, which was not as soluble as antimony trichloride. Stannic chloride and the trichlorides of arsenic and phosphorus were miscible with many of the solvents without causing decomposition; with some solvents reaction did occur. Phosphorus trichloride, it is well known, reacts with many organic solvents forming substitution-products. Whenever chemical action was made apparent by the formation of precipitates or liberation of gases the solutions were not further tested.

Ferric chloride was prepared by passing anhydrous chlorine gas over pure iron wire contained in a heated hard glass tube. Cupric chloride was prepared in an analogous manner. Stannous and aluminum chlorides were obtained by passing dry hydrochloric acid gas over the respective metals contained in heated tubes of glass. The trichloride of antimony was prepared by treating the metal with dry chlorine in a small retort of good glass, with addition of heat, and then distilling the product. Trichloride of bismuth was formed by treating hydroxide of bismuth with concentrated hydrochloric acid,

evaporating to a thick syrup and allowing the mass to cool. The latter was then broken up, the pieces were transferred to a retort of Berlin porcelain, and the product purified by distillation. All of these chlorides were pure and perfectly anhydrous. The mercuric chloride was the C. P. sublimed preparation of Kahlbaum. The stannic chloride was an anhydrous product obtained from Schuchardt. Arsenic trichloride was prepared by treating arsenious acid with dry hydrochloric acid gas in a retort and purifying the product by distillation. It had a very constant boiling-point. The trichloride of phosphorus was a sample obtained from Kahlbaum. It was redistilled and had a very constant boiling-point.

In presenting the results the qualitative determinations will be given first. We found it necessary to make these determinations in order to find out solutions that conduct sufficiently to make quantitative investigations profitable; and as a large number of solvents were tested, it will prove of value to give the results, especially as they cast light upon the question of the cause of the dissociative power of solvents (considering for the present that electrical conductivity of the solution is always caused by electrolytic dissociation).

In this qualitative, or very roughly quantitative, work the plan of experimentation was as follows: In the circuit of a large Leclanché cell were placed a rheostat, a fairly delicate galvanometer and a resistance cell (of the type devised by Arrhenius) into which the solutions tested were introduced. The electrodes of the cell were about four millimeters apart. It was seldom that any of the plugs of the rheostat had to be pulled out, as the resistance in the cell was generally so large that but a small throw of the galvanometer needle resulted in most cases on closing the circuit. The circuit was closed only for a second or two in each case. Of course in operating thus with a direct current polarization could not be avoided; it was the sole purpose of these experiments, however, to find out whether a current could be made to pass through the solution, and if so whether the conduction was sufficient to make it desirable to attempt an exact quantitative determination.

In each case the solvent was first tested as to whether it would conduct. It was found that nearly all the solvents were excellent insulators. In the case of acetic aldehyde and furfurol a slight deflection of the galvanometer needle was observed; in the case of most of the other solvents absolutely no motion of the needle was noted, while in a few instances a mere trace of movement was discernible on closing the circuit. The solvents were all of the C. P. varieties of standard makes, — Schuchardt, Kahlbaum, Merck or Trommsdorf. Prof. Kremers, of the pharmacy department of this university, kindly furnished us several compounds from his collection. Prof. Hillyer, too, was kind enough to place at our disposal a number of preparations in his possession. We desire here to express our thanks to both of these gentlemen for thus furthering our experimental work.

The salts used in making these rough, preliminary tests of conductivity were ferric chloride, antimony trichloride, mercuric chloride and bismuth trichloride. In nearly all of the solvents the order of the solubility of these salts proved to be that just given, ferric chloride being the most soluble. Without exception, the ferric chloride solutions conducted better than the others. We soon found it useless to try solutions of the other three salts if the solutions of ferric chloride did not conduct. After the solvent had been tested in the resistance cell, the salt solutions were likewise tested. The latter were frequently prepared by introducing a little of the salt directly into the solvent contained in the cell. This was the method used whenever the salt dissolved readily; when such was not the case, the solution was prepared in a small test-tube, frequently with the aid of heat; it was then rapidly cooled, introduced into the cell and tested. The strength of the solutions was not accurately ascertained; it varied from about one to five percent.

The results of these tests are given in Table I. The first two columns contain the names and formulae of the solvents. In the next four columns is indicated the electrical conductivity of the solutions of the salts whose formulae head the columns.

When the solution conducted so poorly that no throw of the galvanometer needle was observed, this is indicated by the minus sign (—). A plus sign (+) indicates that the solution did conduct. The addition of the interrogation point to the plus sign (+?) indicates that only a very slight movement of the needle was observed, and the addition of the exclamation point to the plus sign (+!) shows that the solution conducted well enough to make a quantitative determination desirable. An idea as to how great a conductivity this is can be obtained by inspecting the results of conductivity determinations of ferric chloride solutions given farther below. In Table I blank spaces indicate that the solutions were not tested, and the letter (i) shows that the salt was found to be insoluble or at least difficultly soluble. The dielectric constants of the solvents, as far as we were able to obtain them from the literature, are given in the seventh column. Finally, the last column contains the coefficients of association of the solvents, as far as we were able to find them in the literature. The coefficients marked R. & S. are taken from the article of Ramsay and Shields, Jour. Chem. Soc. **63,** 1089 (1893); R. & A. refers to the work of Ramsay and Aston, Ibid. **65,** 168 (1894); D. & F. refers to Dutoit and Friedrich (l. c.).

In addition to the results in the following table, it was found that stannic chloride in arsenic trichloride does not conduct, and phosphorus trichloride in arsenic trichloride does not conduct. Mercuric chloride in arsenic trichloride conducted a little, but when phosphorus trichloride was added to the solution the conductivity diminished to such an extent that the galvanometer needle did not stir. The action of the phosphorus trichloride in the latter case in diminishing the conductivity is possibly analogous to that of alcohol when added to an aqueous solution that conducts.

Looking over the results in Table I it appears that ferric chloride dissolved in hydrocarbons or their halogen substitution products does not conduct. This is in perfect harmony with what others have found regarding solutions of other salts in solvents of this nature. The low dielectric constants and coeffi-

TABLE I

Solvent	Formula	$FeCl_3$	$SbCl_3$	$BiCl_3$	$HgCl_2$	Dielectric constant (air = 1)	Coefficient of association
Heptane	C_7H_{16}	—					
Amylene	C_5H_{10}	—				2.301 Landolt & Jahn	0.96 R. & S. (Schiff)
Benzene	C_6H_6	—				2.3377 Palaz	1.01 R. & S.
Toluene	C_7H_8	—				2.3648 "	
Xylene	C_8H_{10}	—				2.2758 Negreano	
Cymene	$C_{10}H_{14}$	—	—			2.4706 "	
Menthene	$C_{10}H_{18}$	—	i				
Chloroform	$CHCl_3$	—				3.95 Thwing	0.94 R. & S. (Eötvös)
Carbon tetrachloride	CCl_4	—				2.2 Tereschin	1.01 R. & S.
Methylene iodide	CH_2I_2	—					
Ethylene chloride	$C_2H_4Cl_2$	—					
Ethylene bromide	$C_2H_4Br_2$	—					0.95 R. & S. (Eötvös)
Monobrom-benzene	C_6H_5Br	—					
Benzyl chloride	$C_6H_5.CH_2Cl$	—					
Benzal chloride	$C_6H_5.CHCl_2$	—					
Benzotrichloride	$C_6H_5.CCl_3$	—					
Acetyl chloride	CH_3COCl	+!	+	i	i	25.30 Thwing 15.40 Drude	1.05 R. & S.
Benzoyl chloride	C_6H_5COCl	+!	+	i	+		
Methyl alcohol	CH_3OH	+!	+!			32.65 Tereschin	3.43 R. & S.
Ethyl alcohol	C_2H_5OH	+!	+!			25.7 Rosa	2.74 R. & S.
Allyl alcohol	C_3H_5OH	+!				21.6 Thwing	1.88 R. & S.
Benzyl alcohol	$C_6H_5.CH_2OH$	+!	+	+	+	10.6 Drude	
Ethylene glycol	$C_2H_4(OH)_2$	+!	+	+	+		2.92 R. & S.
Glycerine	$C_3H_5(OH)_3$	+!	+	+	+	16.5 Drude	1.80 D. & F.
Epichlorhydrin	C_3H_5OCl	+	+	+	+		
Phenol	C_6H_5OH	+	+	—	+	9.68 Drude	1.42 R. & A.
Meta-cresol	$C_6H_4.CH_3OH$	+	—	—	+(?)		
Ethyl ether	$(C_2H_5)_2O$	—				4.373 Donle	0.99 R. & S.
Phenyl methyl ether	$C_6H_5.O.CH_3$	+	—	i	—		
Acetic anhydride	$(CH_3CO)_2O$	+	+(?)	—			0.99 R. & S.
Acetic aldehyde	CH_3COH	+!	+!	+	+	18.55 Thwing	
Chloral anhydride	CCl_3COH	—	—			5.47 "	1.02 R. & S.
Paraldehyde	$C_6H_{12}O_3$	+!	+	+	+		0.85 R. & S.
Benzaldehyde	$C_6H_5.COH$	+!	+			14.48 Thwing	0.97 R. & S.
Cinnamic aldehyde	$C_6H_5.C_2H_2COH$	+	+	i	+		
Furfurol	$C_5H_4O_2$	+!	+!	+	+	39.4 Drude	
Acetone	$(CH_3)_2CO$	+!	+!			21.85 Thwing	1.26 R. & S.
Methyl-propyl ketone	$CH_3.C_3H_7.CO$	+!	+!	+!	+!	16.75 "	1.11 R. & S.
Aceto-phenone	$CH_3COC_6H_5$	+!	+!	+	+!	16.24 "	1.10 D. & F.
Ethyl acetate	$CH_3COOC_2H_5$	+!	+			6.5 Tereschin	0.99 R. & S.
Ethyl monochloracetate	$CH_2ClCOOC_2H_5$	+!	+	+	+		
Ethyl cyanacetate	$CH_2CN.COOC_2H_5$	+!	+	+	+	26.7 Drude	
Ethyl aceto-acetic ester	$CH_3CO.CH_2COOC_2H_5$	+!	+	+	+	15.7 "	0.96 R. & S.
Propyl acetate	$CH_3COOC_3H_7$	+				6.3 Tereschin	
Butyl "	$CH_3COOC_4H_9$	+				5.0 Drude	
Propyl propionate	$C_2H_5COOC_3H_7$	+					
Amyl butyrate	$C_3H_7COOC_5H_{11}$	+(?)					
Amyl valerianate	$C_4H_9COOC_5H_{11}$	+(?)					
Ethyl benzoate	$C_6H_5COOC_2H_5$	+				6.5 Tereschin	
Ethyl oxalate	$(COO.C_2H_5)_2$	+!	+	+	+		
Ethyl carbonate	$CO(OC_2H_5)_2$	—		—			
Ethyl chlorcarbonate	$CO\,Cl.OC_2H_5$	+!	+!	+	+!		
Ethyl nitrate	$C_2H_5NO_3$	+!	+	i	i	17.72 Thwing	
Amyl nitrite	$C_5H_{11}NO_2$	+!	+	i	+		
Nitro-benzene	$C_6H_5NO_2$	+!	+	+	+	32.19 Thwing 25.58 "	0.93 R. & S. 1.13 R. & S.
o-Nitro-toluene	$C_6H_4.CH_3NO_2$	+!	+	+	+		
Aniline	$C_6H_5NH_2$	+(?)	i	i	+(?)	7.5 Tereschin 7.15 Drude	1.05 R. & S.
Methyl aniline	$C_6H_5NHCH_3$	+(?)	i	i	+		
Dimethyl "	$C_6H_5N(CH_3)_2$	+(?)	i	i	i		
Benzyl amine	$C_6H_5.CH_2NH_2$	+	i	i	+		
Toluidine (ortho)	$C_6H_4.CH_3.NH_2$	+(?)	+(?)	+(?)	i		
Toluidine (meta)	$C_6H_4.CH_3NH_2$	+(?)	+(?)	+(?)	i		
Xylidene (meta asym.)	$C_6H_3.(CH_3)_2.NH_2$	i	i	i	i		
Phenylhydrazine	$C_6H_5.NH.NH_2$	—	i	i	i		
Benzonitrile	$C_6H_5.CN$	+!	+!	+	+	26.0 Drude	0.97 R. & S. 1.02 R. & S.
Pyridine	C_5H_5N	+	i	i	+		0.93 R. & S.
Piperidine	$C_5H_{11}N$	i	i	i	+(?)		1.08 R. & S.
Quinoline	C_9H_7N	+	i	i	+		0.81 R. & S.
Carbon disulphide	CS_2	—				2.61 Palaz	1.07 R. & S.
Phosphorus trichloride	PCl_3	i	—	i	—		1.02 R. & S.
Arsenic trichloride	$AsCl_3$	+!	+	+(?)	+		
Tin tetrachloride	$SnCl_4$	i	i	i	i		

cients of association (as far as available) will be noted in this connection. The acid chlorides, acetyl and benzoyl chloride, do yield solutions that conduct. The dielectric constant of acetyl chloride is much higher than that of chloroform for example, though the results of Thwing and Drude (see table) do not agree. The coefficient of association of acetyl chloride is nearly unity; this shows that there is practically no polymerization of the molecules in the liquid state.

The alcoholic solutions (including glycol and glycerine) conduct sufficiently to make quantitative determinations desirable. The dielectric constants of these solvents are relatively higher and the coefficients of association indicate that the solvents contain polymerized molecules. The viscosity of the solutions of glycol and glycerine no doubt diminishes their conductivity. Solutions in phenol and cresol did not conduct as well as alcoholic solutions. The dielectric constant of phenol is not as high and the coefficient of association is not as great as in the case of the alcohols.

The ethers and even acetic anhydride proved to have but slight dissociative power. Their molecules are not polymerized and the dielectric constant of ether is low.

Acetic aldehyde yielded solutions that conducted fairly well relatively; one would expect this from the dielectric constant found by Thwing (see Table I). On the other hand solutions in chloral did not conduct, which fact harmonizes with the low dielectric constant of this substance. The molecules of chloral are not polymerized as the table shows; unfortunately the coefficient of association of aldehyde has not been determined. Paraldehyde has considerable dissociative power in spite of the fact that its coefficient of association indicates that its molecules are not polymerized. Benzaldehyde solutions of ferric chloride conducted sufficiently to make quantitative measurements desirable (see results below); the dielectric behavior of this solvent is such as to lead one to expect this. The molecules of this solvent are not polymerized according to the determinations of Ramsay and Shields. Solutions in cinnamic aldehyde did not

conduct very well; but those in furfurol were found to conduct very well relatively. The high dielectric constant of this substance will be noted in this connection.

The three ketones tested yielded solutions that conduct well. This was to be expected from their dielectric constants. It will be observed, however, that their coefficients of associations are such as to indicate but very slight polymerization of their molecules.

Among the esters, ethyl acetate, in spite of its low dielectric constant (compare the same with that of chloral), yielded solutions that conduct (see measurements below). Solutions in monochloracetate of ethyl seemed to conduct about the same and the cyanacetate did not appear to yield better conducting solutions in spite of the fact that it contains the CN group and has a relatively high dielectric constant. Aceto-acetic ester solutions of ferric chloride conducted well relatively (see determinations below), though its dielectric constant is only 15.7,[1] and its coefficient of association shows that its molecules are not polymerized. The solutions in propyl acetate, butyl acetate and ethyl benzoate conducted but slightly; their dielectric constants are low. However, since the dielectric constant of butyl acetate is rather lower than that of chloral one would expect the ferric chloride solution of the former to show no conductivity. Ferric chloride in propyl propionate conducted slightly, while its solutions in amyl butyrate and amyl valerianate showed but the slightest movement of the galvanometer needle. The dielectric constants of these solvents are probably also low, though they have, to our knowledge, not been determined. The solutions in ethyl oxalate conducted fairly well; but those in ethyl carbonate, in spite of the high oxygen content of this solvent, did not conduct noticeably at all. Again, ethyl chlorcarbonate yielded solutions that conducted well relatively.

The results obtained by using nitrogen compounds as solvents are of particular interest. Ethyl nitrate, amyl nitrite, nitrobenzene and nitrotoluene it will be noted yielded solutions

[1] That of ethyl cyanacetate is 26.7.

that gave a fair degree of conduction (see determinations for nitrobenzene solutions below). The dielectric behavior of these solvents would lead one to expect this. The molecules of nitrobenzene are, according to Ramsay and Shields, not polymerized. In aniline, methyl- and dimethylaniline, and in benzylamine, ferric chloride is quite soluble but the solutions conduct very poorly indeed. The benzylamine solutions seemed to conduct a little better than the others. In the toluidines ferric chloride was not readily soluble; only a very slight deflection of the galvanometer needle was observable on testing the solutions. Xylidine did not dissolve the salts tested, as shown in the table. Only the dielectric constant of aniline was found in the literature. This constant is low and one would expect low dissociative power. The molecules of aniline are not polymerized, according to the coefficient of association. Although phenylhydrazine dissolves ferric chloride readily, the solution so obtained does not conduct; not the slightest movement of the galvanometer needle was observable. Benzonitrile yielded solutions that conducted very well. This is in harmony with the results of Dutoit and Friedrich, that solutions in nitriles conduct well. The relatively high dielectric constant of benzonitrile will be noted; on the other hand, its coefficient of association is so low as to show that its molecules are not polymerized. Pyridine yielded solutions that conduct. St. v. Laszczynski u. St. v. Gorski[1] determined the conductivity of solutions of salts of the alkalies in this solvent. It will be noted that its molecules are not polymerized. Piperidine did not dissolve the salts tested appreciably, except in the case of mercuric chloride. The conductivity of this solution was very slight. The coefficient of association of this solvent indicates no polymerization. Quinoline yielded solutions that conducted slightly. Its molecules are not polymerized. The dielectric constants of the last three bases appear not to have been determined thus far.

Carbon disulphide solutions of ferric chloride do not con-

[1] l. c.

duct, which is in harmony with the low dielectric constant of this solvent whose molecules are also not polymerized.

Antimony trichloride dissolves readily in phosphorus trichloride, but the solution does not conduct; neither does the solution of mercuric chloride in phosphorus trichloride conduct. The coefficient of association of phosphorus trichloride shows that its molecules are not polymerized.

Ferric chloride dissolved in arsenic trichloride, conducts fairly well, and the solutions of the other three salts in this solvent conduct, but not as well.

The rule that the greater the dielectric constant of the solvent, the greater is its dissociative power, holds in general. A few apparent deviations were noted above.

Since only the hydroxyl derivatives in Table I have coefficients of association that indicate polymerization of their molecules, and since the solutions they yield are by no means the only ones that conduct electricity, it is clear that the theory[1] that only those solvents whose molecules are polymerized possess dissociative power is untenable.

In summing up the relations between the chemical composition of the solvent and its dissociative power, it appears that solutions in hydrocarbons or their halogen substitution-products do not conduct. Alcoholic solutions conduct well comparatively. The higher the carbon content of the alcohol, the less is its dissociative power. The hydroxyl derivatives of the aromatic series possess less dissociative power than those of the fatty series; this is especially true when the hydroxyl group occurs in the benzene ring. Ethers and acid anhydrides do not possess dissociative power, or possess it only in a slight degree. The behavior of carbon disulphide would indicate that this possibly holds true also for other sulphur compounds.[2] Aldehydes on

[1] Compare Dutoit and Aston, l. c. Also Dutoit and Friedrich, l. c. The influence of viscosity on the conductivity, upon which the latter insist, can not be doubted.

[2] As a matter of fact, Werner, Zeit. anorg. Chem. **15**, 39 (1897), found that cuprous chloride, though fairly soluble in methyl sulphide, conducts very poorly in that solvent.

the whole yield solutions that conduct relatively well. This cannot be ascribed solely to the presence of the aldehyde group, for solutions in chloral do not conduct. Here is a case where substitution of chlorine for hydrogen is accompanied by a reduction of dissociative power. On the other hand, when in acetic- or benzaldehyde the hydrogen of the aldehyde group is replaced by chlorine, the acid chlorides result and the compounds do not lose their dissociative power. When the hydrogen of the aldehyde group is replaced by an alkyl radical, the resulting compounds, the ketones, retain dissociative power. Esters have slight dissociative power on the whole, which decreases as their carbon content increases. Substitution of Cl, CN or $CH_3.CO$ for one of the hydrogens of the methyl group does not cause the compound to lose its dissociative power. (In the latter instance it has been found to increase it.) Ethyl carbonate does not yield conducting solutions, but when one of its ethoxy groups is replaced by chlorine the solvent becomes endowed with dissociative power. This shows that it would not be correct to make the general statement that substitution by halogen in a compound has a tendency to reduce dissociative power. The nitrogen compounds containing oxygen combined with that element possess dissociative power. The amido compounds of the aromatic series have but very slight dissociative power. Phenylhydrazine yields a non-conducting solution of ferric chloride. Nitriles yield conducting solutions, as do also ring compounds containing nitrogen. The trichloride of phosphorus does not have dissociative power, while the opposite is true of arsenic trichloride.

Finally, how do these results agree with the theory of Brühl? In the case of all the compounds containing oxygen there would be an abundance of spare valences because Brühl regards oxygen as tetravalent. In general it has been found to be true that oxygen compounds do possess dissociative power. But chloral, ethyl carbonate and ethers[1] have no dissociative power, while esters with high carbon content yield solutions

[1] Compare also the remarks of Dutoit and Friedrich, l. c.

that practically do not conduct. Again when chlorine is substituted for an ethoxy group, the number of spare valences is certainly reduced (assuming oxygen to be a tetrad), nevertheless solutions in ethyl chlorcarbonate conduct well. The amido compounds yielded solutions that conducted but very slightly, contrary to Brühl's prediction. Perhaps he would characterize the amido compounds tested as not sufficiently active. Again the phenylhydrazine solution did not conduct. Of course it remains for future experimentation to show what hydrazine will do. Substitution of CN for hydrogen in ethyl acetate did not seem to affect the dissociative power much. Solutions of antimony trichloride, mercuric chloride, stannic chloride and arsenic chloride in phosphorus trichloride did not conduct. This too is contrary to Brühl's prediction. Solutions in arsenic trichloride did conduct as Brühl predicted. Solutions of cuprous chloride in methyl sulphide conduct very poorly according to Werner's[1] determination; this is also contrary to Brühl's expectation. On the whole it is evident that Brühl's theory is in many instances not supported by the facts, and consequently it must be pronounced untenable.

The results of the accurate measurements of the electrical conductivity will now be given together with the molecular weight determinations, when such have been made. The conductivity was measured in each case according to the method of Kohlrausch, the results being given in reciprocal mercury units. A cell patterned after that of Arrhenius was used. It had a tightly fitting cover so as to exclude the moisture of the air as much as possible. The determinations were made at 25° C unless otherwise indicated. In no case has the conductivity of the solvent been deducted. It has in each case been determined, however. The cryoscopic determinations were made with Beckmann's apparatus, all the usual precautions being taken. In the tables of electrical conductivity v indicates the volume in liters in which one gram-molecule is contained, and μ the molecular conductivity.

[1] l. c.

SOLUTIONS IN METHYL ALCOHOL

The solvent was the C. P. commercial article. It was distilled twice from anhydrous copper sulphate after having stood over this substance for several days. Finally it was treated with metallic sodium, distilled and again redistilled. Its boiling-point was then quite constant, and its specific conductivity was 5.7×10^{-6}.

TABLE II

Solvent: methyl alcohol

Ferric Chloride, $FeCl_3$				Antimony Trichloride, $SbCl_3$			
v	μ	v	μ	v	μ	v	μ
3.20	20.81	102.48	60.55	8.15	15.68	260 96	89.47
6.41	25.26	204.96	72.61	16.31	18.94	521.91	118.34
12.81	31.09	409.91	89.11	32.62	28.52	1043.83	156.32
25.62	40.90	819.83	111.08	65.24	43.32		
51.24	49.00	1639.66	147.08	130.48	63.33		

SOLUTIONS IN ETHYL ALCOHOL

This solvent was prepared in the same manner as was methyl alcohol. Its boiling-point was quite constant also. Its specific conductivity was found to be 7.7×10^{-9}.

TABLE III

Solvent: ethyl alcohol

Ferric Chloride, $FeCl_3$				Antimony Trichloride, $SbCl_3$			
v	μ	v	μ	v	μ	v	μ
2.89	9.91	46.28	15.51	8.11	4.18	129.81	18.23
5.79	13.06	92.56	16.69	16.23	5.68	259.62	29.43
11.57	13.70	195.12	19.33	32.45	7.94		
23.14	14.50	390.24	21.20	64.91	12.30		

SOLUTIONS IN ACETONE

The solvent was a C. P. commercial sample. It was allowed to stand over fused calcium chloride for over two weeks. Finally it was redistilled four times from fused calcium chloride. It then had a very constant boiling-point. Its specific conductivity was 5.4×10^{-6}. In this solvent bismuth trichloride was practically insoluble.

TABLE IV

Solvent: acetone

Ferric Chloride, $FeCl_3$		Antimony Trichloride, $SbCl_3$		Cupric Chloride, $CuCl_2$		Stannous Chloride, $SnCl_2$	
v	μ	v	μ	v	μ	v	μ
14.65	51.70	7.07	1.23	45.87	25.72	37.78	8.77
29.30	59.90	14.14	1.55	91.74	27.10	75.56	8.09
58.60	64.65	28.27	1.83	183.48	28.71	113.33	6.87
117.19	68.68	56.56	2.13	366.96	28.94		
234.39	70.67	113.10	3.34	733.91	29.18		
468.77	72.28						
937.54	83.76						
1875.08	91.22						

SOLUTIONS IN ETHYL ACETATE

The solvent was of the C. P. variety. It was treated repeatedly with anhydrous copper sulphate from which it was distilled each time. Finally it was redistilled, when it showed a constant boiling-point. Its specific conductivity was 4.5×10^{-7}.

TABLE V

Solvent: ethyl acetate

Ferric Chloride, $FeCl_3$		Antimony Trichloride, $SbCl_3$		Stannous Chloride, $SnCl_2$		Bismuth Trichloride, $BiCl_3$	
v	μ	v	μ	v	μ	v	μ
16.89	0.87	10.92	0.013	68.05	0.042	112.12	0.034
33.78	1.12	21.84	0.019				
67.46	1.25						

SOLUTIONS IN ETHYL ACETOACETATE

This solvent was a product obtained from Schuchardt. It was subjected to fractional distillation. A sample which boiled between 174° and 176° C at 736 mm, was used in the experiments. Its specific conductivity was 4×10^{-8}.

TABLE VI

Solvent: ethyl acetoacetate

Ferric Chloride, $FeCl_3$		Antimony Trichloride, $SbCl_3$		Bismuth Trichloride, $BiCl_3$		Arsenic Trichloride $AsCl_3$	
v	μ	v	μ	v	μ	v	μ
5.46	10.82	0.75	0.031	5.65	0.059	0.47	0.087
15.04	14.04	0.94	0.034	11.31	0.053	0.65	0.071
16.31	14.08	1.34	0.041	27.09	0.098	0.84	0.068
22.14	14.62	2.76	0.044	48.20	0.137	1.13	0.067
24.12	14.63	4.34	0.050	83.00	0.164	1.37	0.067
27.59	15.04	8.18	0.059	288.96	0.472	2.49	0.084
31.90	15.25	17.02	0.076	Mercuric Chloride, $HgCl_2$		3.50	0.070
44.64	15.94	36.69	0.108			10.20	0.085
157.98	19.79	59.86	0.132	v	μ	31.13	0.114
240.51	20.65	511.50	0.529	0.91	0.012	Stannic Choride, $SnCl_4$	
503.56	23.43	Phosphorus Trichloride, PCl_3		1.35	0.013		
				2.91	0.017	v	μ
		v	μ	36.33	0.072	2.02	1.08
		1.80	0.026			4.13	1.71
		4.48	0.097			8.76	2.37

TABLE VII

Ferric Chloride in Ethyl Acetoacetate

($v = 5.46$ at 25° C. Solution two weeks old).

t	μ	t	μ	t	μ	t	μ
25° C	12.0	60° C	18.2	75° C	20.7	90° C	21.7
50	16.8	65	19.2	81	21.2	95	21.8
56	17.5	70	19.9	86	21.7	100	21.7

(At higher temperatures gases are rapidly disengaged from the solution.)

SOLUTIONS IN BENZALDEHYDE

This solvent was prepared by Schuchardt. It was redistilled. A sample boiling between 177° and 178° at 741 mm was used in the experiments. Its specific conductivity was 4.5×10^{-7}.

TABLE VIII

Solvent: benzaldehyde

Ferric Chloride, $FeCl_3$		Antimony Trichloride, $SbCl_3$			
v	μ	v	μ	v	μ
25.58	14.32	1.96	0.12	33.10	0.86
51.65	14.58	2.42	0.14	62.52	1.24
117.91	13.05	3.51	0.17	155.22	1.68
157.79	12.14	5.80	0.28	523.39	2.62
237.14	10.50	14.89	0.48		

TABLE IX

Ferric Chloride in Benzaldehyde

($v = 25.58$ at 25° C)

t	μ	t	μ	t	μ	t	μ
25° C	14.3	65° C	23.1	85° C	26.4	105° C	24.1
52	20.5	70	24.3	90	26.4	111	24.0
55	20.9	75	25.1	95	24.5	125	24.0
60	22.1	80	25.9	102	24.1		

SOLUTIONS IN NITROBENZENE

This solvent was from Kahlbaum. It was prepared from crystallizable benzene. Its specific conductivity was 3.5×10^{-7}.

TABLE X

Solvent: nitrobenzene

Ferric Chloride, $FeCl_3$				Antimony Trichloride, $SbCl_3$		Arsenic Trichloride, $AsCl_3$	
v	μ	v	μ	v	μ	v	μ
2.84	3.76	181.49	18.86	1.83	0.023	1.338	0.016
5.67	4.79	362.98	20.02	3.65	0.048	2.676	0.021
11.34	6.58	725.96	20.51	7.31	0.122	4.014	0.028
22.68	13.70	1451.93	20.82	14.60	0.225	Phosphorus Trichloride, PCl_3	
45.37	16.25	2903.86	20.45	29.21	0.390	v	μ
90.74	17.61			58.41	0.706	8 43	0.026
				116.83	1.276	16.86	0.042

TABLE XI

Ferric Chloride in Nitrobenzene

($v = 7.189$ at 25° C)

t	μ	t	μ	t	μ	t	μ
25° C	5.2	70° C	9.2	95° C	12.5	130° C	16.4
52	7.2	75	9.8	100	13.3	135	16.7
56	7.6	80	10.3	110	14.6	140	16.8
61	8.1	85	11.0	123	15.7	145	16.9
67	8.8	90	11.6	125	15.9	150	16.9

The following cryoscopic determinations in nitrobenzene solutions are of interest in connection with the results of the measurements of the electrical conductivity. The solvent used in these determinations was that already described. It was, how-

ever, recrystallized several times in this case before being used. The molecular lowering of the freezing-point used in the calculations was 70.70 (Compare Ostwald's *Grundriss der allgemeinen Chemie*).

TABLE XII

Solvent: nitrobenzene

Substance in 100 g solvent	Lowering	Mol. wt.
Ferric Chloride, $FeCl_3$. Mol. Wt. = 161.14		
1.4792	0.330°	316.9
1.6510	0.433	269.6
1.9661	0.575	241.7
2.3582	0.728	229.2
3.0566	1.065	203.0
3.4823	1.255	196.2
4.0097	1.501	188.9
4.7389	1.756	190.8
Antimony Trichloride, $SbCl_3$. Mol. Wt. = 225.06		
2.5811	0.714°	255.6
3.1528	0.910	245.5
5.2983	1.585	236.3
6.3113	1.928	231.4
7.2706	2.248	228.7
8.3095	2.625	223.3
10.6533	3.555	211.9
Stannic Chloride, $SnCl_4$. Mol. Wt. = 258.87		
2.1259	0.337°	445.9
3.4059	0.742	332.1
5.3896	1.242	306.8
6.8268	1.662	290.4
Arsenic Trichloride, $AsCl_3$. Mol. Wt. = 179.98		
0.3997	0.223°	126.7
0.9756	0.493	139.9
1.2298	0.568	153.1
1.7010	0.763	157.6
2.7756	1.189	156.1
3.7299	1.554	169.7
4.5366	1.857	172.7
5.2582	2.138	174.3
6.4207	2.613	173.7
7.8651	3.179	174.9
10.4542	4.207	175.7
Bismuth Trichloride, $BiCl_3$. Mol. Wt. = 312.08		
0.6833	0.230°	203.9
0.9190	0.250	258.1
1.1268	0.280	282.6
1.4927	0.340	301.8
1.8563	0.410	317.9
3.0829	0.662	326.9
Phosphorus Trichloride, PCl_3. Mol. Wt. = 136.33		
0.9339	0.530°	124.6
1.3482	0.758	125.8

The relatively high values of μ for ferric and antimony chlorides in methyl alcohol (Table II) and also their great increase with the dilution, showing no tendency toward a maximum will be noted. The figures remind one of the behavior of ferric chloride in aqueous solutions, where hydrolytic decomposition occasions great increase of conductivity with increase of dilution. In ethyl alcohol (Table III) the conductivity of these salts is very much less. The values of μ for ferric chloride

show relatively less change with increasing dilution, while those of antimony trichloride increase more rapidly with the dilution than in the corresponding solutions in methyl alcohol.

In acetone (Table IV) the values of μ for ferric chloride are higher than in methyl alcohol, except at the higher dilutions. The low conductivity of antimony trichloride in acetone as compared with its conductivity in methyl or even ethyl alcohol is striking. Cupric chloride dissolved in acetone conducts well. The values of μ change but little with the dilution and appear to tend towards a maximum. Stannous chloride shows a rather low molecular conductivity when dissolved in acetone. The values of μ show a decrease with the increase of dilution.

In ethyl acetate (Table V) the conductivity of the various salts was uniformly low.

In ethyl acetoacetate (Table VI) the values of μ for ferric chloride are, roughly speaking, of the order that they are in ethyl alcohol solution (Table III). The relatively slight change of the conductivity with the dilution will be noted. The change of the conductivity with the temperature too is of interest (Table VII). At first μ increases with the temperature, but the change per degree grows less as the temperature rises, finally (at about 86°) becoming practically nil.[1] The low values of μ for all the other salts in ethyl acetoacetate will be noted. It is especially interesting that antimony trichloride here, as in acetone, gives a very low value for μ as compared with that of ferric chloride.

In benzaldehyde antimony trichloride conducts but slightly (Table VIII). Ferric chloride has a much greater conductivity, which shows a decrease with increase of dilution. The change of μ for the ferric chloride solution with the temperature is interesting (Table IX). At first there is a gradual increase up to about 90° or 95°; then there is a slight decrease, the values soon becoming constant.

[1] Dutoit and Friedrich (l. c.) found that cadmium iodide dissolved in acetonitrile, or acetone shows no variation of μ with the dilution or with the temperature. They incline to ascribe this behavior to a combination between the solvent and the dissolved substance.

In nitrobenzene (Table X) the conductivity of all the solutions except that of ferric chloride is low. The values of μ for the latter become practically constant at the higher dilutions. The conductivity of a ferric chloride solution (Table XI) increases steadily with the temperature until about 130° C has been reached, when it becomes constant.

The cryoscopic determinations in nitrobenzene solutions (Table XII) indicate that the molecular weight of ferric chloride is uniformly higher than the theoretical, and that it decreases with increase of concentration of the solution. This decrease of molecular weight with increase of concentration is also to be observed in case of the solutions of antimony trichloride, though here the variation is much less relatively and the more concentrated solutions show a molecular weight slightly below the theoretical. Stannic chloride behaves like ferric chloride in that the molecular weight is greater than the theoretical and that it decreases with increase of concentration of the solution. The trichlorides of bismuth, arsenic and phosphorus in dilute solutions give molecular weights that increase with the concentration of the solutions. In the more dilute solutions the values are lower than the theoretical.

As the molecular weights of the chlorides of iron, antimony and tin in nitrobenzene increase with the dilution, it is clear that the number of dissolved molecules must decrease with the dilution. A simple polymerization of the molecules of the respective salts, seems here excluded, as it would naturally decrease rather than increase with the dilution. Some combination with the molecules of the solvent such that the total number of dissolved molecules suffers a reduction, therefore seems to take place. If this assumption be made, it is clear that electrolytic dissociation might still take place to a certain extent in the solution and yet the cryoscopic results be such as they are.

Dutoit and Friedrich[1] state that they have found normal molecular weights by the boiling-point method for the compounds of the formulæ $CNS.NH_4$, $HgCl_2$, NaI, LiCl, CdI_2,

[1] l. c.

when dissolved in acetone. These solutions conduct electricity well. The authors claim that this behavior is not in contradiction to the dissociation theory. Their explanation is to appear later.

A Werner[1] has made molecular weight determinations of inorganic salts in pyridine, benzonitrile, methyl sulphide, ethyl sulphide, and piperidine by the boiling-point method. He finds as a general result that his determinations indicate little or no dissociation of the salts tested. The latter included, among others, silver nitrate, mercuric iodide and mercuric chloride in benzonitrile, and silver nitrate and ferric chloride in pyridine. The calculated molecular weight of silver nitrate is 170; in benzonitrile it was found to be 176, and in pyridine 165.42[2]. Again the calculated molecular weights of mercuric iodide and mercuric chloride are 454 and 271 respectively; in benzonitrile they were found to be 474 and 300 (in another series 238) respectively. It must be added that Werner does not claim a very high degree of accuracy for these results. We have not made accurate determinations of the electrical conductivity of the solutions just mentioned, but we have tested them roughly and know that they do conduct very well. It is not easy to explain from the standpoint of the dissociation theory why they should conduct well and still yield molecular weights that are normal or nearly so. Accurate measurements are of course necessary before the extent of the discrepancy, which apparently exists, can be determined. When solutions of silver nitrate and mercuric iodide in benzonitrile are mixed there is formed momentarily a curdy precipitate that has every outward appearance of silver iodide. This fact would indicate that silver and iodine ions are present in the solutions. It remains to be seen whether the degree of ionization is sufficient to account for the conductivity. Unfortunately the amount of benzonitrile we have on hand is not sufficient to investigate this matter at once.

Werner[3] has isolated and analyzed addition-products of

[1] Zeit. anorg. Chem. **15,** 1 (1897).

[2] The averages of several experiments are given here.

[3] l. c.

piperidine with inorganic salts. He states that the molecular weight determinations of these salts in piperidine solutions are but slightly influenced by the fact that piperidine can form addition-products with the salts. This appears to be analogous to the fact that a salt, although it is capable of crystallizing with one or more molecules of water, yields the same molecular weight whether dissolved as anhydrous salt or with its crystal water. We desire to quote a sentence from Werner in this connection: "*Da nicht bezweifelt werden kann, dass in bestimmten organischen Lösungen hydratähnliche Additions-producte von Lösungsmittel und Metallsalz als beständige Verbindungen gelöst sind, so muss auch angenommen werden, dass bestimmte Hydrate in den wässerigen Lösungen enthalten sein können; wenn im letzterem Fall eine elektrolytische Dissoziation eintritt, so entstehen nicht Metallionen, sondern an deren Stelle treten ionisierte Metallwasserradikale.*" While we do not think that Werner's argument warrants drawing this conclusion, yet the sentence seems very suggestive.

It would to our minds prove rather premature to try to decide at this time whether the dissociation theory in its present form can account for the conductivity and other properties of solutions of salts in solvents other than water, for the experiments performed by us and by others are as yet too few to warrant broad generalization. This paper, moreover, is only preliminary in character. From the results above detailed, it seems safe to say that different solvents act differently on one and the same salt. The general outlook at present appears to be that in order to harmonize the molecular weight determinations in many non-aqueous solutions with the relatively high electrical conductivity of the latter, the assumption that combination between solvent and dissolved substance takes place, will have to be made. Can it be true that after its glorious success in explaining the properties of aqueous solutions of acids, bases and salts, the dissociation theory will need the help of its old rival, the hydrate theory (perhaps in somewhat modified form), to explain the facts in the case of non-aqueous solutions? Further diligent

experimental investigation only can definitely answer this question. We need not only to know the molecular weights of the dissolved substances and the electrical conductivity of the solutions, but we need to know whether the reactions that take place in them are momentary; in other words, whether they are ionic reactions, as in the case of aqueous solutions. The behavior of non-aqueous solutions upon electrolysis, their optical and other properties must be studied. The potentials of the galvanic chains in which these solutions are used as the electrolytes, must be investigated.

The electrolysis of non-aqueous solutions and the potentials that exist between the metals and non-aqueous conducting solutions of their salts are being studied in this laboratory. Further work on conductivity and molecular weight determinations is also in progress.[1]

Laboratory of Physical Chemistry,
University of Wisconsin,
Madison, Dec. 19, 1898.

[1] Since the above was written, Prof. Bancroft in a letter to us directed our attention to the theory of Konowalow (Wied. Ann. **49**, 733, 1893) that a solution conducts only when there is a chemical reaction between solvent and dissolved substance. The work was done on salts of the amines. Referring to Konowalow's work Bancroft wrote :—"These experiments are not conclusive because aniline and acetic acid both conduct a little in water and there is always a possibility of dissociation into $C_6H_5\overset{+}{N}H_3$ and $CH_3C\overset{-}{O}O$. In view of this hypothesis, would it not be a good plan to try the conductivity of picric acid in benzene? Benzene picrate exists in solution and it would certainly be a very surprising phenomenon if it should be an electrolyte. As it would take you but a little while to settle the question one way or the other, it would seem worth while to make the determinations." Among many other tests, the results of which have not been published, we had tried the conductivity of picric acid in benzene some weeks before Prof. Bancroft's letter arrived, but we have again repeated the test with the same result that picric acid in benzene does not conduct. Not the slightest movement of the galvanometer needle could be observed (see plan of experimentation above). The result simply shows that chemical action between solvent and dissolved substance may take place and yet the solution formed need not necessarily conduct electricity.

BOILING-POINT CURVES

BY E. F. THAYER

In a recent number of the Journal[1] I have described the boiling-point curve for mixtures of benzene and alcohol. Since then I have extended the investigation and have studied mixtures of chloroform and alcohol, acetone and alcohol, acetone and chloroform. The apparatus used was that of Orndorff and Cameron.[2] The thermometer was made by Gerhardt and was graduated to tenths of a degree, the scale being so large that hundredths could be estimated without difficulty. In all the determinations only a relatively short portion of the mercury column was out of the vapor. No correction has been applied for this. The boiling-points were determined at atmospheric pressure and efforts were made to select such times for the experiments as to have the pressure practically constant at least for each set of readings. The errors introduced from this source are believed to be unimportant.

The alcohol used was dried over lime for two weeks and then distilled from it. It then stood in contact with dehydrated copper sulfate for some days, was decanted and distilled with a Hempel column. The product distilled at a constant temperature. The first and last portions were discarded. The chloroform was washed repeatedly with water in order to remove the alcohol, traces of which were found to remain even after long standing over calcium chlorid. After being washed the chloroform was kept for two days in contact with calcium chlorid, then decanted and distilled from fresh calcium chlorid. It then distilled at a constant temperature. The distillate was

[1] Jour. Phys. Chem. **2**, 382 (1898).
[2] Am. Chem. Jour. **17**, 517 (1895).

then redistilled with a Hempel column, all distilling at 60.4°. The first and last portions were discarded. The acetone was kept in contact with calcium chlorid, for some days, then decanted and distilled from fresh calcium chlorid. It distilled at 55.25°–55.75°. It was then distilled with a Hempel column, the first and last portions being discarded. It distilled constantly at 55.7°.

The measurements were made in the manner described in the previous paper. The results are given in the following tables, the temperatures being all uncorrected.

TABLE I

Alcohol and Chloroform

Alcohol percent	Temp	Bar	Alcohol percent	Temp	Bar
100.00	77.86°	744.2	40.05	63.32°	744.2
89.13	75.61	744.2	34.62	62.18	744.2
74.62	72.10	744.2	28.89	61.03	744.2
67.14	70.19	744.2	19.51	60.19	744.2
57.77	67 69	744.2	13.06	59.39	744.2
50.92	65.93	744.2	7.09	59.09	744.2
46.54	64.78	744.2	0.00	60.93	744.2

From these figures it appears that the curve passes through a minimum. In order to determine the position of this minimum more exactly the following series of determinations was made.[1]

TABLE II

Alcohol and Chloroform

Alcohol percent	Temp	Bar	Alcohol percent	Temp	Bar
0.00	60.50°	732.5	9.31	58.65°	732.5
2.60	59.06	732.5	14.54	59.08	732.5
6.37	58.57	732.5	19.01	59.55	732.5

From these data it is clear that the mixture with constant boiling-point contains about seven percent of alcohol, the boiling-temperature being about 58.5° under a pressure of 732.5 mm of mercury.

[1] By F. K. Cameron.

TABLE III

Acetone and Alcohol

Acetone percent	Temp	Bar	Acetone percent	Temp	Bar
100.00	55.6°	742.9	45.31	63.42°	739.1
91.82	56.58	742.9	40.86	64.22	739.1
85.46	57.30	742.7	36.74	65.13	739.4
77.43	58.39	742.7	30.08	66.79	739.4
66.92	59.80	742.4	26.02	67.92	739.4
60.99	60.72	742.2	17.86	70.51	739.4
53.93	61.82	742.2	11.41	72.83	739.4
45.50	63.29	741.9	0.00	77.70	739.4

The boiling-point curve has neither a maximum nor a minimum and presents no unusual feature.

TABLE IV

Acetone and Chloroform

Acetone percent	Temp	Bar	Acetone percent	Temp	Bar
100.00	55.38°	736.4	40.74	61.66°	735.8
86.42	56.48	736.4	35.29	62.27	735.8
75.96	57.51	736.1	29.83	62.77	735.7
69.57	58.21	736.1	24.09	63.21	735.6
63.24	58.94	736.1	20.34	63.32	735.5
56.09	59.77	736.0	18.19	63.30	735.5
50.38	60.47	735.8	9.31	62.48	735.5
46.08	61.00	735.8	0.00	60.39	735.6

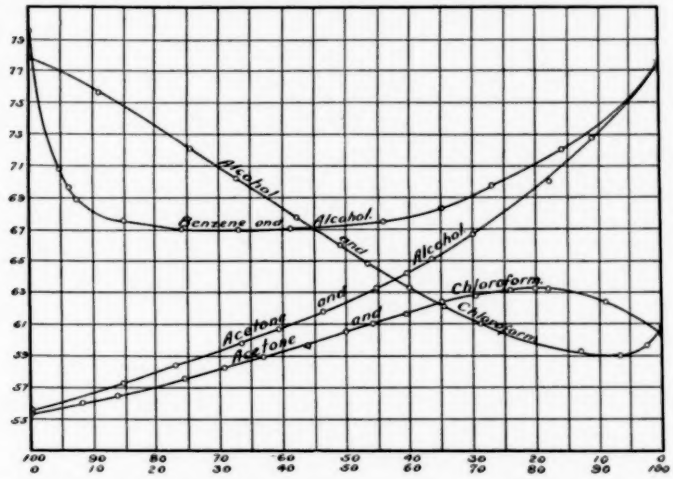
Repeated fractional distillation yielded a mixture which boiled constantly at 63.4° under a pressure of 737.1 mm of mercury. By interpolation this mixture was found to contain approximately nineteen percent of acetone. The curve for acetone and chloroform, when plotted, seemed to be a trifle wavy near the acetone end. This was verified by the following experiments.

TABLE V

Acetone and Chloroform

Acetone percent	Temp	Bar	Acetone percent	Temp	Bar
100.00	55.51°	740.2	67.60	58.55°	740.2
89.66	56.35	740.2	48.08	60.91	740.2
80.10	57.22	740.2	43.22	61.60	740.2

The results given in the tables are also represented graphically in Fig. 1. The curve for benzene and alcohol is also re-



produced for purposes of comparison. In the diagram the ordinates are temperatures and the abscissas are percentage compositions by weight. To avoid confusion the curves are labelled and the substance for which the left-hand ordinate denotes one hundred percent is placed first. The chloroform and alcohol curve is distinctly wavy near the alcohol end; the acetone and chloroform is wavy, though not markedly so, at the acetone end.[1] The curve for benzene and alcohol cuts the curve for chloroform and alcohol in spite of the difference between the boiling-points of benzene and chloroform.

Lehfeldt[2] has recently determined the pressure-concentration curve for benzene and alcohol at 50°. He finds that the solution having the highest vapor-pressure contains twenty-seven to twenty-eight percent of alcohol. This differs a good deal from my value of thirty-three and one-half percent at 66.5°.

[1] The waviness of the curves does not show perceptibly in the cut owing to the smallness of the scale.

[2] Phil. Mag. [5] **46**, 42 (1898).

While it is not impossible that the position of the maximum should be displaced six percent by a change in temperature of 16.5°, this is so much in excess of the displacement observed with aqueous solutions of the halid acids that it seems more reasonable to attribute some of the difference to experimental error. This seems the more probable because the curve in this particular case happens to be so flat that it is not easy to determine the position of the maximum by interpolation. In my experiments the solution having the minimum boiling-point was determined by means of fractional distillation, thus eliminating the necessity for interpolation.

The experimental work described in this paper was carried out under the supervision of Dr. Frank K. Cameron. The general results of the investigation are:

1. A mixture of benzene and alcohol containing 33.5 percent. of alcohol distils without change at 66.7° under a pressure of 737 mm of mercury.

2. A mixture of chloroform and alcohol containing about 7 percent of alcohol distils without change at 58.5° under a pressure of 732.5 mm of mercury.

3. A mixture of chloroform and acetone containing about 19 percent of acetone distils without change at 63.4° under a pressure of 737.1 mm of mercury.

4. The boiling-points of all mixtures of alcohol and acetone lie between the boiling-points of pure alcohol and pure acetone.

Cornell University

REVERSIBLE REACTIONS

BY JOHN WADDELL

In a paper by Walker and Hambly[1] on the conversion of ammonium cyanate into urea they state that it is capable of easy mathematical proof that in a *reversible* monomolecular reaction the form of the differential equation is the same as in the case of a reaction running to the end in one direction, the difference being that the equilibrium point is used instead of the original active mass. In the ordinary nomenclature instead of the formula $\frac{dx}{dt} = k(A - x)$ the formula to be used is $\frac{dx}{dt} = k_1(\xi - x)$. Walker and Hambly do not show the relationship between k and k_1 but merely by integration obtain the equation

$$\frac{1}{t} \log \frac{\xi}{\xi - x} = \text{const.}$$

They found that in the case in hand the values obtained were not constant and they therefore proceeded to calculate the constant on the basis of the reaction being bimolecular, simply remarking "neglecting as in the previous case the slow reverse action by taking the value of the end point as the original active mass we find the expression $\frac{1}{t} \frac{x}{\xi - x}$ is indeed constant".

In another paper I have given a mathematical proof of the first statement which holds strictly no matter where the point of equilibrium may be, but in endeavoring in the same way to confirm the formula for a reverse bimolecular reaction I found that I could not do so. In trying to discover in what manner Walker and Hambly arrived at their conclusion the following mode of treating the subject occurred to me.

Assuming that the equations suggested are correct, let us

[1] Jour. Chem. Soc. **67**, 753 (1895).

find what conditions must be fulfilled. For a reversible monomolecular reaction the equation is

$$\frac{dx}{dt} = k_1(\mathrm{A} - x) - k_2 x,$$

where k_1 and k_2 are the reaction velocities in the two directions. But according to the assumption

$$\frac{dx}{dt} = k_3(\xi - x)$$

where ξ is the equilibrium point and k_3 is some constant so far unknown. We have therefore

$$k_1(\mathrm{A} - x) - k_2 x = k_3(\xi - x)$$

or

$$k_1\mathrm{A} - k_1 x - k_2 x = k_3\xi - k_3 x.$$

Equate coefficients of like power of x and we have

$$k_1\mathrm{A} = k_3\xi \text{ and } k_1 + k_2 = k_3.$$

It remains to be seen whether these equations are consistent and for this purpose we may make use of the relation between k_1 and k_2 obtained from the conditions of equilibrium where

$$k_1(\mathrm{A} - \xi) - k_2\xi = \frac{dx}{dt} = 0$$

since at equilibrium the rate of change is zero. This equation gives

$$k_1\mathrm{A} = (k_1 + k_2)\xi$$

which exactly coincides with the value obtained from the two equations of condition. It follows therefore that in this case our assumption is completely justifiable.

In the simplest case of a reversible bimolecular reaction we have

$$\frac{dx}{dt} = k_1(\mathrm{A} - x)^2 - k_2 x^2$$
$$= k_3(\xi - x)^2$$

according to our assumption. Expanding

$$k_1\mathrm{A}^2 - 2k_1\mathrm{A}x + k_1x^2 - k_2x^2 = k_3\xi^2 - 2k_3\xi x + k_3x^2$$

whence by equating coefficients of like power of x

$$k_1A^2 = k_2\xi^2, \quad 2k_1A = 2k_2\xi \text{ and } k_1 - k_2 = k_3.$$

From the first of these equations of condition $\frac{k_1}{k_2} = \frac{\xi^2}{A^2}$ and from the second $\frac{k_1}{k_2} = \frac{\xi}{A}$. This can be true only when $\xi = A$ in which case the reaction will run to the end, and when $\xi = o$ in which case the reaction will not go on at all.

It would appear from the paper by Walker and Appleyard[1] that while the change from ammonium cyanate into urea is considered bimolecular the reverse action is taken as monomolecular. This assumes that

$$\frac{dx}{dt} = k_1(A - x)^2 - k_2x = k_3(\xi - x)^2$$

from which by expanding and equating as before the equations of condition are

$$k_1A^2 = k_2\xi^2, \quad 2k_1A + k_2 = 2k_3\xi, \quad k_1 = k_3.$$

From the first and third of these equations $\xi^2 = A^2$; therefore $\xi = \pm A$. The negative value is meaningless; the positive value as in the other case means that the reaction runs to the end and is not reversible.

After I had worked out the problem as above, I found that Ostwald[2] has gone into the matter very fully and for a reverse monomolecular reaction gives the equation

$$\frac{dx}{dt} = (k_1 + k_2)(C - x).$$

He works out C in terms of k_1, k_2, and A, and shows incidentally without laying stress upon the point that this last expression is equal to ξ.

The reversible bimolecular equation

$$\frac{dx}{dt} = k_1(A - x)^2 - k_2x^2$$

may be thrown into another form which will show to what ex-

[1] Jour. Chem. Soc. **67**, 753 (1896).

[2] Lehrbuch II, **2**, 251 and ff (1897).

tent Walker and Hambly were wrong in their assumption. Expanding and arranging the powers of x

$$\frac{dx}{dt} = (k_1 - k_2)\left(x^2 - \frac{2k_1A}{k_1 - k_2}x + \frac{k_1A^2}{k_1 - k_2}\right)$$

$$= (k_1 - k_2)\left(x - \frac{k_1A}{k_1 - k_2}\left(1 + \sqrt{\frac{k_2}{k_1}}\right)\right)\left(x - \frac{k_1A}{k_1 - k_2}\left(1 - \sqrt{\frac{k_2}{k_1}}\right)\right)$$

as may be proved by putting

$$x^2 - \frac{2k_1A}{k_1 - k_2}x + \frac{k_1A^2}{k_1 - k_2} = 0$$

and solving the equation.

If $\frac{k_2}{k_1} = a$ then $k_1 - k_2 = k_1(1 - a)$ and the equation becomes

$$\frac{dx}{dt} = k_1(1 - a)\left(x - \frac{A}{1 - a}(1 + \sqrt{a})\right)\left(x - \frac{A}{1 - a}(1 - \sqrt{a})\right)$$

$$= k_1(1 - a)\left(x - \frac{A}{1 - \sqrt{a}}\right)\left(x - \frac{A}{1 + \sqrt{a}}\right)$$

$$= k_1(1 - a)(x - \xi_1)(x - \xi_2),$$

where ξ_1 and ξ_2 are the values of ξ obtained from the equation of equilibrium

$$\frac{k_2}{k_1} = \frac{(A - \xi)^2}{\xi^2}$$

from which

$$\pm\sqrt{\frac{k_2}{k_1}} = \pm\sqrt{a} = \frac{A - \xi}{\xi}$$

whence

$$\xi = \frac{A}{1 \pm \sqrt{a}}.$$

Since the conditions of the experiment necessitate that ξ shall be positive and not greater than A the value $\xi = \frac{A}{1 + \sqrt{a}}$ is the only possible one under the circumstances. This is the value designated ξ_2. Nevertheless the value ξ_1 is calculable and must be taken into account. The equation of Walker and Hambly

was $\frac{dx}{dt} = k(x-\xi)^2$, where they regard k as a constant without showing its relation to the velocity coefficients. This form coincides with the one above only when $\xi_1 = \xi_2$, in which case it is easily seen they are both equal to A, that is the reaction is not a reversible one. Ostwald[1] arrives at a formula which differs from that which I have worked out in that he has omitted the factor $(1-a)$. He quotes from Guldberg and Waage,[2] but in modifying their form has left out the factor named.

Integrating the expression

$$\frac{dx}{dt} = k_1(1-a)\left(x - \frac{A}{1-\sqrt{a}}\right)\left(x - \frac{A}{1+\sqrt{a}}\right)$$

between the limits $x = 0$ and $x = x$ and $t = 0$ and $t = t$ we obtain

$$ln\,\frac{x(1-\sqrt{a})-A}{x(1+\sqrt{a})-A} = 2A\sqrt{a}\,t.$$

Using ordinary logarithms we have

$$\frac{1}{t}\log\frac{x(1-\sqrt{a})-A}{x(1+\sqrt{a})-A} = \text{const.}$$

The following table shows the constant obtained by Walker and Hambly's calculation and that worked out according to the preceding formula

$$A = 25 \quad \xi = 22.9 \quad \frac{A-\xi}{\xi} = \sqrt{a} = \frac{2.1}{22.9}$$

t	x	$\xi - x$	$\frac{1}{t}\frac{x}{\xi-x}$	$\frac{1}{t}\log\frac{x(1-\sqrt{a})-A}{x(1+\sqrt{a})-A}$
45	4.4	18.5	0.00528	0.000377
72	6.5	16.4	0.00549	0.000389
107	8.3	14.6	0.00529	0.000370
157	10.1	12.8	0.00502	0.000344
230	12.3	10.6	0.00505	0.000335
312	14.2	8.7	0.00524	0.000337
600	17.2	5.7	0.00502	0.000297

Cornell University

[1] Lehrbuch II, **2**, 256.

[2] Jour. prakt. Chem. [2] **19**, 81 (1879).

NEW BOOKS

Das Leitvermögen der Elektrolyte. *By F. Kohlrausch and L. Holborn. 15 × 22 cm; pp. xvi and 211. Leipzig: B. G. Teubner, 1898. Price 5 marks.* — The publication of this book marks a new era in conductivity measurements. Hence forward determinations of resistance will be given in ohms instead of mercury units. One of the things that has stood in the way of this change to a rational basis has been the mass of data already accumulated that had either to be recalculated or thrown away. The authors have gone to infinite trouble and have recalculated everything, making such corrections as seemed advisable owing to errors in the standards adopted by different workers. The book contains a short chapter on instruments for measuring resistance; an excellent and relatively long chapter on the Kohlrausch method of determining resistances; a chapter on solutions in general, including methods of preparing and diluting solutions; a discussion of migration, transference numbers, dissociation and dissociation formulas; a statement of the conductivity in other solvents and a dissertation on water. There is also a chapter on temperature, including baths and temperature coefficients as well as one on the chemical applications of conductivity measurements, under this head coming the analysis of concentrated and dilute solutions and solubility determinations.

Seven pages of fine print are devoted to the literature of the subject and then come nearly seventy pages of tables. There are tabulated: specific conductivity of aqueous solutions of salts, bases and acids at 18°; equivalent conductivity of inorganic compounds at 18° and at 25°; molecular conductivity of inorganic acids and bases at 25°; equivalent conductivity of organic salts at 25°; molecular conductivity of organic acids and bases; temperature coefficients; migration velocities; transference numbers; volume determinations with water or mercury; stability of salts, and water of crystallization; solubility of salts in water at 18°; conductivity of standard solutions; atomic weights; equivalent weights and electrochemical equivalents of univalent and bivalent ions; Obach's tables for the Wheatstone bridge giving ratios and the logarithms of the ratios; a short table of four-place logarithms.

It is unnecessary to praise this book, for it takes the place of all that has been done heretofore in conductivity determinations and is therefore indispensable. The reviewer wishes, however, to call special attention to the statement on p. 103 that the transference numbers in general are not independent of the concentration. It is usually assumed that the transference numbers are independent of the concentration in moderately dilute solutions. A glance at the table on p. 201 shows that silver nitrate and possibly hydrochloric acid are the only substances for which the effect of concentration can be said to have

disappeared in tenth-normal solutions. While this may be due to experimental error, as is usually assumed to be the case, this has not yet been shown.

When the second edition is issued the reviewer would suggest that the van 't Hoff and Rudolphi dissociation formulas be referred to immediately after the Ostwald formula. It would also increase the value of the literature index if references were given to the pages in the book where the papers are mentioned. If this should not be deemed practicable there should at least be a name index. The absence in this edition of both name and subject index is an unfortunate blemish in an otherwise admirable book. *Wilder D. Bancroft*

The Discharge of Electricity through Gases. *By J. J. Thomson. 13 × 19 cm; pp. x and 203. New York: Charles Scribner's Sons, 1898. Price: cloth $1.00.* — The popular opinion among chemists, so far as they have any opinion on the subject at all, is that electricity does not pass through gases in any proper sense of the word; but rather that it jumps. This little volume containing the lectures delivered by J. J. Thomson at Princeton in October of 1896 will therefore come as a surprise and a pleasure to many. It is full of most interesting facts and in reading it one fluctuates between amazement that so much has been done without attracting the attention of chemists and sorrow that there should still be so little in the way of connected theory. The main facts are clear enough. Gases, including vapors, do not become charged by contact with a charged substance; nor is the passage of liquid into vapor accompanied by electrification. On the other hand gases given off during chemical reaction or during electrolysis are charged and the mean charge per unit mass is said to be of the same order as the charge passing with unit mass in an electrolytic solution. Gases can also be charged by being splashed by liquids. Exposure to Röntgen rays or to uranium radiation makes a gas able to receive a charge. We have quantitative measurements on the rate of leak and on the application of Ohm's law to gases; we have abundant evidence as to distinct electrolytic action in gases and, more interesting still, we have many experiments on the things that one can do with a charged gas. In many cases the gas will pass through glass wool or bubble through solutions without losing its charges, while if it is blown through the walls of a porous cup, the charge will stay behind. This makes very interesting reading even without the chapter on the cathode rays; but all through one feels the lack of a guiding hypothesis. The subject has now been developed to such an extent that it is no longer profitable to make scattered observations. It is interesting to study science as a sporting-dog hunts birds; but no man can become a leader unless he has or appears to have some goal in sight.

The time is certainly ripe for at least a tentative hypothesis in regard to the discharge of electricity through gases, and while the physical chemist has, as yet, done little work in this field there should be no one better qualified to attack the problem. Whoever takes up this line of work will find this book of great assistance and the volume should be read with care by all interested in physical chemistry regardless of whether they intend to do special work in the subject or not. *Wilder D. Bancroft*

Die moderne Entwicklung der electrischen Principien. *By F. Rosenberger. 15 × 22 cm; 170 pp. Leipzig: Johann Ambrosius Barth, 1898. Price: paper 3 marks.* — The author is already favorably known through his history of physics and his life of Newton. Like these, the five lectures embodied in the book before us are fascinatingly written, and though popular are addressed to students of rather broad culture in physical science. The book is obviously an outgrowth from original sources, and the author's method of presenting the cardinal advances in electrical science in the language of the great thinkers themselves is a clever accomplishment. It will be difficult to find anywhere a more concise and lucid presentation of the great debt which electrical science owes to Franklin, for instance. Franklin is so thoroughly identified with the lightning rod that one is apt to overlook his really great achievement: for he it was who propounded the first thoroughgoing theory from a modern (Maxwellian) point of view by which electrical science profited. The contributions of Faraday are reviewed with equal vigor; and even though these and the work of Maxwell are familiar to English readers, the chapters repay perusal. The book ends with an able discussion of the trend of modern science from dynamic to kinetic methods. It contends that opposed theories do not necessarily stand to one another in the relation of absolute truth to absolute error: that both rather correspond to successive stages of development, and at a given time may very well be in the same degree relatively true. *C. Barus*

Maassanalytische Studien. *By Julius Wagner. 14 × 21 cm; 123 pp. Leipzig: Oskar Leiner, 1898.* — The book is divided into three fairly distinct parts: the general sources of error in volumetric analysis; standardizing iodometric solutions; the reaction between potassium permanganate and hydrochloric acids in presence of ferrous salt. In the first part we find, among other interesting things, a discussion of the differences due to blowing out a pipette or letting it drain. The author is very strongly of the opinion that the requirements of the Reichsanstalt are not sufficiently rigorous with regard to the calibration of pipettes and he believes that for pipettes, burettes, and flasks the limit of permissible error should not exceed 0.1 percent in guaranteed instruments. The reviewer is glad to see that the use of floats in burettes is condemned. In order to reduce the error in using burettes to a minimum the author recommends preparing standard solutions at a temperature of 20° so that fluctuations in temperature during measurements shall have relatively little effect. For normal solutions a change of temperature from 15° to 25° introduces an error of 0.2–0.3 percent, a point that is sometimes overlooked. A further recommendation is that burettes should be calibrated uniformly and used with a correction table, since an attempt to eliminate the variations in diameter by correspondingly irregular calibration usually introduces as much of an error as it eliminates, so that one gets no value for the extra cost of such instruments.

In the second part of the book the author shows that sodium thiosulfate solutions can be standardized to within 0.1 percent. Potassium bi-iodate and potassium bromate are the best substances for this purpose; but under no circumstances is it safe to use either of these salts without further purification, no matter from whom they were bought. Potassium bichromate is not suitable

because it accelerates the reaction between hydriodic acid and the oxygen of the air so that more iodin is precipitated than should be

The conclusions reached in the third part of this work are summed up as follows:

The error in the reaction between potassium permanganate and hydrochloric acid in presence of ferrous salts is probably due to the temporary formation and rapid oxidation of a chloroferrous acid.

Salts of chromium, cadmium, etc., produce the same result as ferrous salts. So also do auric and platinic chlorids. In the case of platinic chlorid it has been shown that chloroplatinic acid is oxidized more rapidly than hydrochloric acid and has a lower decomposition voltage. Through freezing-point determinations the gradual formation of a chlorocadmic acid was established.

The presence of barium chlorid introduces an error that may amount to 45 percent. For the apparent increase in reaction velocity due to secondary reactions the author proposes the term pseudocatalysis. *Wilder D. Bancroft*

Commercial Organic Analysis. *By Alfred H. Allen. Third Edition, Revised and Enlarged; Vol. I, 16 × 23 cm; pp. xii and 557. Philadelphia: P. Blakiston's Son and Co., 1898. Price: cloth $4.50.* — The following extract from the note to the third edition of this book explains the reason for the publication of a new edition of this very valuable work. "The last edition of this volume, issued in 1885, and which has been out of print for several years, was recently reprinted *under the date of 1898, without the permission of the author and without revisions;* and as this unauthorized reprint necessarily misrepresented Mr. Allen's present views on many subjects, he determined to issue a revised edition immediately. While everything has been done to make the book up to date, the exigencies of the occasion limited the time that could be allotted for revision, and distance prevented submission of any manuscript or proof-sheets to the author".

Comment on the conduct of a publishing house which would publish a work printed in 1885 under the date of 1898 without the author's permission and entirely without revision is unnecessary here. It is to be hoped that American chemists will not encourage such dishonesty to the author and the reading public by purchasing the unauthorized edition of the book. This new edition of Allen's Organic Analysis has long been needed and will be most heartily welcomed by every chemist, who has anything to do with the analysis of organic substances. Mr. Allen has furnished material for the new edition on the following subjects: Kjeldahl process; proteids of wheat flour; vinegar; brewing sugars; malt substitutes; hop substitutes and the secondary constituents in spirits. The work done by the American revisor has been necessarily limited. He has, however, done his part very well and has added information on the following subjects, partly from suggestions by Mr. Allen: specific gravity; formaldehyde; vinegar; methyl alcohol; acetone; fusel oil; argol; starch; glucose; invert sugar; lactase; and wine. A particularly good idea of the American revisor was the incorporation in this edition of the processes of the American Association of Official Agricultural Chemists. "Bulletin 46" of the Association is now out of print. It will therefore be of great advantage to the analytical and technical chemist to have these processes where they can readily be found.

The book is well printed and bound and is very free from errors of every kind. For the analytical and technical chemist the book is simply indispensable. *W. R. Orndorff*

Outlines of Industrial Chemistry. *By F. H. Thorp. 15 × 23 cm; pp. xvii and 541. New York: The Macmillan Co., 1898. Price: cloth $3.50.*—The treatment in a volume of this size of the large number of subjects which are ordinarily included under the title of Industrial Chemistry, is a difficult task indeed and the author is to be congratulated upon the success of his attempt. The first half of the book treats of the most important inorganic chemical industries with the exception of metallurgy, which is very properly entirely omitted. The second half is given over to the organic industries which are treated quite fully with the exception of the coal-tar dyestuffs which are limited to seven pages of the nature of a catalogue of the various dyestuffs. One cannot help thinking that these pages might better have been used for some other purpose.

The chemical side of the subject is very properly most strongly emphasized and the mechanical helps are only treated, in so far as they are necessary for an intelligent understanding of the various processes. The mechanical treatment is for the most part up to date although in some cases older machines are described while the more modern ones are omitted. This is especially noticeable in the case of burners for pyrites "smalls" where the almost obsolete Perret-Ollivier, Gerstenhofer, and Hasenclever-Helbig burners are discussed and the modern Spense, and Frasch mechanical burners are not even mentioned.

The chemical portion is well up to date and the treatment is clear considering the necessity for brevity, while numerous references to other sources of information supplement the text.

The table of contents is worthy of mention as it is so comprehensive that it affords a means of determining at a glance just what is treated under each head. The book also contains a very satisfactory index. *F. L. Kortright*

Les Recettes du Distillateur. *By E. Fierz. 13 × 19 cm; 149 pp. Paris: Gauthier-Villars et Fils, 1899. Price: paper 2.75 francs.*—The first eighteen pages are devoted to a general statement. The alcohol, sugar and water used must all be pure and it is especially important that the sugar should not be bluish in color since this denotes an impurity of ultramarine which would impart an odor of hydrogen sulfid to the liqueurs. A list is given of the taste and odor of different vegetable ingredients and detailed directions are given for preparing and keeping syrups, coloring matters and alcoholic extracts. The rest of the book is devoted entirely to formulas for preparing liqueurs, creams, bitters, punches and brandies. The scope of the book may be inferred from the fact that one hundred and fifty preparations are discussed. The author says that if his directions are followed exactly there will be no difficulty in making good liqueurs, though the best results can be obtained only by keeping the liqueurs at least a year. *Wilder D. Bancroft*

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry

General

On thermokinetic properties of thermodynamic potentials. *L. Natanson. Zeit. phys. Chem.* **24,** *302* (*1897*).—The author applies the thermokinetic principle to a system whose state is determined by the values of unspecified independent variables p; and their differential coefficients according to the time, and makes the same assumptions as in Zeit. phys. Chem. **21,** 153 (**1,** 374) except that the "impossible and unnecessary" conditions that the differential of work is done in an exclusively reversible manner, is dropped. Consequently the variations of the work δw, as in the case of the heat δQ, are divided into a reversible and an irreversible part. In this way a general equation is obtained from which the general thermokinetic Lagrangian equations are directly deduced. Next, the variables are more specified, one being chosen as the absolute temperature θ, the other q_i remaining general. The thermokinetic principle applied to this case leads to an equation which falls into two parts one of which does not contain the variable θ and is termed "the isothermal form of the thermokinetic principle". A general function V of q_i and θ is defined, of which, under special assumptions, the free energy is a special case. By making the definite assumption that $\delta^{\circ}Q$ (the reversible part of δQ) is equal to $\theta\delta S$, the entropy S is introduced and a modified form of the isothermal thermokinetic principle obtained. Lastly the system is considered in which the independent variables are still more specialized. They are θ, the reversible part of all the dynamic coefficients P_k° and sufficient other unspecified variables m_h to completely define the system at any moment. Application of the thermokinetic principle yields an equation from the three parts of which the corresponding Lagrangian equations are deduced. The third part contains only the variables m_h and is termed "the isothermal-isodynamic form of the thermokinetic principle". A general function Ω analogous to V is introduced, of which, under special assumption the "so-called complete thermodynamic potential" Φ is a special case. The three Lagrange equations referred to above in which Φ is introduced "express the thermokinetic properties of this function".

F. B. K.

On some non-reversible processes. *A. Wassmuth. Wied. Ann.* **62,** *522* (*1897*).—A mathematical treatment of a system in which so-called friction and viscosity forces occur. As illustration of this result the representation of elec-

trical and magnetic phenomena by Maxwell's equations is quoted and the deduction of the latter given. *F. B. K.*

On alterations of state in a moving system. *L. Natanson. Zeit. phys. Chem.* **26,** *285 (1898).* — A lengthy mathematical investigation of the laws governing a system consisting of two completely immiscible and mutually freely transformable homogeneous phases in a state of motion. [The condition of immiscibility seems, in view of the assumed "free mutual transformation", to lack physical significance.] The treatment is based on the use of the author's "thermokinetic principle". At the end of the article the author gives one illustration of the application of the results in the case of a piece of ice partly dipping into a stream of water and finds that if the particles at a point in the surface of the water close to the line of contact with the ice have a velocity of one meter per second, a temperature difference of about 1/2000° must prevail near the line of contact. The practical application of the results to any useful physico-chemical problem is not obvious. *F. B. K.*

Review: on action at a distance. *P. Drude. Wied. Ann.* **62,** *693 (1897).* — "Action at a distance is said to exist between two bodies A and B spatially separated from each other when A exerts an action on B without other bodies effecting a continuous material connection between them". According as the word "action" is construed in a purely mechanical sense or in the more general sense, as applying to alterations of condition, the definition of action at a distance will include (a) attraction of mass, forces between electrified bodies, forces between magnetized bodies, electromagnetic and electrodynamic action, or, in addition, (b) phenomena of the induced electric current (in as far as the current strength is characteristic for the condition of the body through which it flows), all phenomena of radiation (in as far, for instance, as temperature or chemical nature can be altered by radiation). With regard to the "continuous material connection", contact action may be brought about either through the medium of *pressure* or by means of *impacts*.

The next section (II) is devoted (a) to a review of the speculative attempts to attribute action at a distance to contact action and (b) to a mathematical consideration of the two classes of action. From the latter point of view the class to which a given phenomenon belongs is simply a question of the practical expediency of taking as starting-point, on the one hand, a differential equation (or set of simultaneous differential equations), or, on the other, the integration of such equations, the latter giving the laws of action at a distance between two points in space.

Section III gives "a comparison of the properties of electromagnetic action and of gravitation". Section IV is a review of investigation on the validity of Newton's law of gravitation, and Section V of the attempts to explain gravitation. The article contains excellent illustrations both of the value and of the worthlessness of an hypothesis. *F. B. K.*

On the thermodynamics of phosphorescence. *K. Wesendonck. Wied. Ann.* **62,** *706 (1897).* — In such phenomena as the rise in temperature of a body at 1° caused by a fluorescing substance at 0° the author sees no contradiction to the principle that heat cannot pass from a colder body to a warmer one, but

simply a direct heating at the cost of "Leuchtenergie". It appears to him also "questionable whether radiation should be treated directly as heat at all". These ideas are, however, not new; and have been clearly set forth by Ostwald (Lehrbuch, 2nd ed. II, **1**, 1011), where there is an explicit warning against assuming that chemical energy, for instance, must first be transformed into heat before it can pass into the form of radiant energy. *F. B. K.*

Permanent changes and thermodynamics. Correction. *P. Duhem. Zeit. phys. Chem.* **24,** *666 (1897).* — A correction to the above article (l. c. **22,** 545) which leaves the result materially unaltered. *F. B. K.*

Recent investigations into the numerical value of "the mechanical equivalent". *E. H. Griffiths. Nature,* **56,** *258 (1897).* — Before a satisfactory comparison between the heat developed by mechanical and electrical means is possible, further data regarding Rowland's mercury thermometer are necessary. The author gives a synopsis of results obtained in the following researches (to be published in America) carried out with a view to supplying this deficiency: (1) a recalculation of Rowland's value of the mechanical equivalent of heat in terms of the Paris hydrogen thermometer, by W. S. Day; (2) a comparison of Rowland's mercury thermometer with Griffiths's platinum thermometer, by C. W. Waidner and F. Mallory. From the results the author draws the following conclusions: (a) that the rate of change in the capacity for heat of water from 10° to 25° may be considered as known with sufficient accuracy for present purposes; (b) that the persistent difference in the capacity for heat of water when determined by mechanical and electrical methods indicates a possibility that there is some error in one of the electrical units — and that, for example, an error of 1 in 1000 in the electrochemical equivalent of silver would account for nearly the whole of our present discrepancies". *F. B. K.*

The electrochemical equivalent of silver. *Lord Rayleigh. Nature,* **56,** *292 (1897).* — Referring to the above article by Griffiths, Rayleigh points out that until 1873 an uncertainty of at least one percent existed in the value for the electrochemical equivalent of silver. In experiments by Mrs. Sidgwick and himself in 1882 an accuracy of 1/2000 was hoped for, although it would, in the author's opinion, "be rash to exclude the question of an error of 1/1000." *F. B. K.*

One-Component Systems

On the question whether the maximum tension of a vapor depends upon the temperature alone. *S. A. Julius. Arch. néerl.* (*2*) **1,** *393 (1898).* — Reviewed (**1,** 596) from Kon. Akad. Wetensch. Verslag. Amsterdam, **1896-97,** 295.

Liquid hydrogen. *Hampson-Dewar Controversy. Nature,* **58,** *55, 77, 125, 174, 199, 246, 270, 292 (1898).* — In Vol. 58 of *Nature* (p. 55) is given a short account of Prof. Dewar's success in the liquefaction of hydrogen. The production of 20 cc of liquid hydrogen was achieved by means of a large plant of the same type as that used for the production of a jet of hydrogen (Roy. Inst. Proc. 1896). "The yield of liquid was about one percent of the gas. The hydrogen in the liquid condition is clear and colorless, showing no absorption spectrum, and the meniscus is as well defined as in the case of liquid air. The liquid must have

a relatively high refractive index and dispersion, and the density must also be in excess of the theoretical value, viz. 0.18 to 0.12. ..." Helium was liquefied by placing a tube containing this gas in boiling hydrogen.

In the following numbers of Nature has appeared a long discussion between Mr. W. Hampson and Prof. Dewar, originated by the former who claims that he has a right to recognition as inventor of the method used by Dewar, to whose assistant he had communicated the plans. Whatever may be the rights about this purely personal controversy — and this it is impossible to decide without reference to other relevant letters in Engineering and Jour. Soc. Arts — it may be remarked that Mr. Hampson's letters at least are characterized by courtesy and fairness of language. *F. B. K.*

Liquid air at one operation. *Lord Rayleigh. Nature*, **58,** *199 (1898).* — Referring to the liquefaction of air by Linde and Hampson, Rayleigh makes a valuable suggestion in calling attention to the fact that "... to allow the work of expansion to appear at the very place where the utmost cooling is desired, is very bad thermodynamics," and suggests that a small turbine might be inserted to carry the work outside the apparatus. *F. B. K.*

Two-Component Systems

On the occlusion of oxygen and hydrogen by platinum-black, II. *L. Mond, W. Ramsay and J. Shields. Zeit. phys. Chem.* **25,** *657 (1898).* — Continuation of a research published in Phil. Trans. **186,** 657 (1895) and Zeit. phys. Chem. **19,** 25 (1896). Owing to the invariable presence of oxygen in platinum-black which it is impossible to remove without destroying the absorption properties of the material, all previous determinations of the heat of absorption of hydrogen in this substance are unreliable as they include the formation of an unknown quantity of water. This difficulty is overcome by allowing hydrogen to be absorbed at the ordinary temperature to convert the oxygen into water, after which it is pumped out at 184° and finally re-admitted to the platinum-black at 0° in an ice calorimeter. An average of four experiments gave the value 137.6 K per gram-molecule of hydrogen. That the heat of absorption for that part of the hydrogen which can be pumped out of the platinum at ordinary temperatures is the same as for the part which is not given off till the temperature 184° is reached disproves the existence of two separate compounds of hydrogen evidenced by Berthelot's results. The latter part of the research is devoted to various estimations of the heat of absorption of oxygen in platinum-black. An average of two direct and three indirect determinations gave 176 K for one gram-atom.

Incidentally the result is arrived at that practically the same volumes of hydrogen, carbon monoxid and sulfur dioxid are taken up by platinum-black, suggesting surface action as explanation of the absorption. On the other hand, the practical identity of the heat of absorption of oxygen with the heat of oxidation (179 K) points strongly to oxidation as the cause in this case.

F. B. K.

On the occlusion of hydrogen and oxygen by palladium. *L. Mond, W. Ramsay, and J. Shields. Zeit. phys. Chem.* **26,** *109 (1898).* — From the absorp-

tion of oxygen by heated palladium-black and from the value of the heat evolution (179.2 K for one gram-atom) the authors conclude that the formation of an oxid PdO probably occurs. The only evidence, on the other hand, for the existence of a chemical combination between hydrogen and palladium is the approximate correspondence of the completely saturated palladium with the formula Pd_3H_2 (H : Pd = 1 : 1.37 to 1 : 47 instead of 1.5). *F. B. K.*

A simple experiment to demonstrate the Ludwig phenomenon. *R. Abegg. Zeit. phys. Chem.* **26,** *161 (1898).* — A description of air apparatus (with figure) by which the alteration in concentration caused in the parts of a homogeneous solution by unequal temperature — usually known as the Soret phenomenon — may be conveniently and quickly demonstrated. The author has unfortunately omitted the dimensions of the apparatus. The relative concentrations in the hot and cold part of the solution are not necessarily inversely proportional to the absolute temperatures, as required by van 't Hoff's interpretation, but may also be influenced by the fact that the coefficient of partition between hot and cold solvent may differ from unity, in evidence for which view the author cites Arrhenius's results reviewed by himself in Zeit. phys. Chem. **26,** 187.

F. B. K.

On the condensation of a mixture of two gases. *J. P. Kuenen. Arch. néerl.* (*2*) **1,** *331 (1898).* — Reviewed (**1,** 690) from Kon. Akad. Wetensch. Verslag, Amsterdam, **1894-95,** 90.

The dissociation of water into oxygen and hydrogen in mixtures of water and alcohol. *R. Luther. Zeit. phys. Chem.* **26,** *317 (1898).* — The author calculates the relative dissociation of water according to the equation

$$2H_2O \rightleftharpoons 2H_2 + O_2,$$

in various mixtures of alcohol and water, using the solubilities of oxygen and hydrogen in these solvents as measures of the active masses. The active mass of the water is measured by the vapor pressures.

"For the validity of the formula used the following are assumed to hold: (1) Boyle's law in high dilution; (2) Dalton's law of independent partial pressures; (3) the Henry-Dalton absorption law in mixed solvents. ..."

One other necessary condition the author appears to have overlooked, namely the validity of the sign $\rightleftharpoons$ in the above equation under the conditions under which the solubilities were determined. To admit this would be to admit the unlimited simultaneous solubility of hydrogen and oxygen in water.

F. B. K.

Poly-Component Systems

Experimental verification of van 't Hoff's constant in very dilute solutions. *M. Wildermann. Zeit. phys. Chem.* **25,** *698 (1898).* — Reviewed (**1,** 739) from Jour. Chem. Soc. **71,** 796 (1897).

Dalton's law in solutions. *M. Wildermann. Zeit. phys. Chem.* **25,** *711 (1898).* — Reviewed (**1,** 742) from Jour. Chem. Soc. **71,** 743 (1897).

On the solubility of iodin in mixed solvents. *L. Bruner. Zeit. phys. Chem.* **26,** *145 (1898)* — Solubility determinations of iodin in mixtures, in

varying proportions, of the following pairs of solvents: C_6H_6 and $CHCl_3$, CS_2 and $CHCl_3$, C_6H_6 and CCl_4, CS_2 and CCl_4, C_2H_5OH and $CHCl_3$, C_3H_7OH and $CHCl_3$, C_2H_5OH and H_2O, C_3H_7OH and H_2O and in solutions of potassium iodid. In all cases the solubility was less than that calculated from the "rule of mixtures". It is a pity, considering the valuable nature of such data that the determinations were not carried out with more pretense to accuracy.

F. B. K.

A new process for obtaining high temperatures and for preparing difficultly fusible metals free from carbon. *T. Goldschmidt. Zeit. Elektrochemie*, **4**, *494 (1898)*. — When aluminum is mixed with a metallic oxid and a portion of the mass heated to the proper temperature the oxid is reduced and the resulting heat causes the reaction to take place throughout the whole mass. By adding small quantities of an oxidizing substance, such as a peroxid, the temperature necessary to start the reaction is lowered. By this method it is possible to reduce large masses of metals like chromium that require a temperature of about 3000°. By taking the oxid in excess the resulting metal contains no aluminum and since it does not come in contact with carbon it does not contain this substance as impurity. The method is also adapted for soldering with hard solder, it being a simple matter to obtain the rise of temperature necessary to fuse the solder. *W. D. B.*

On soluble gold. *R. Zsigmondy. Zeit. Elektrochemie*, **4**, *546 (1898)*.— When a dilute solution of gold chlorid is made slightly alkaline and treated with formaldehyde, colloidal gold is obtained and the red solution can be concentrated and freed partially from the other substances by dialysis. With increasing concentration the gold precipitates as black powder on the membrane, becoming gold color when dry. Addition of sodium chlorid or dilute acids to a dialyzed gold solution causes a sudden change to blue and then a precipitation of purplish-black gold. Fungi have the power to absorb colloidal gold. On mixing solutions of colloidal gold and colloidal stannic acid and precipitating with salt the purple of Cassius is obtained. Mercury does not act on a solution of colloidal gold. *W. D. B.*

Osmotic Pressure and Diffusion

Note on the kinetic theory of solutions. *A. A. Noyes. Zeit. phys. Chem.* **24**, *366 (1897)*. — A correction of a false interpretation, Ibid. **23**, 61, of a statement of Nernst. *F. B. K.*

Lord Rayleigh's proof of van 't Hoff's osmotic theorem. *F. G. Donnan. Nature*, **57**, *53 (1897)*. — By an addition to Rayleigh's proof (**1**, 607) the restriction to involatile solvents is avoided. The author shows, further, that even the assumption of Boyle's law for the gas is not required and that the equation $pv = PV$ is a formal consequence of the distribution-law and the expressibility of p as an infinite power series of the density. *F. B. K.*

Velocities

On the rate of saponification of the esters of polybasic acids. *O. Knoblauch. Zeit. phys. Chem.* **26**, *96 (1898)*. — Ostwald's theory of the saponification of

the esters of dibasic acids (Lehrbuch, 2nd ed., **2**, II, pp. 277–281), according to which the reaction may be expressed by the assumption of two stages: (1) formation of the salt of the ester acid; (2) formation of the complete salt is experimentally verified in the case of ethyl succinate and sodium hydrate for ordinary temperature. From the two independent differential equations obtained by applying the mass law to each stage of the reaction a relation between the concentrations of the alkali and ester (C_a, C_e) and the two equilibrium constants (K_1K_2) is obtained. To verify this relation C_a was determined experimentally as a function of the time, while K_1 and K_2 were estimated respectively from observations of the C_a near the beginning and near the end of the process, in both of which cases the reaction is practically an ordinary bi-molecular one. C_e could not be determined directly but was obtained with the help of the equation $\frac{dp_e}{d\theta} = -K_1C_aC_e$ from the value of K_1 and the graphical integration of $C_a d\theta$ from the experiments. In that way C_a was calculated and found to agree well with the observed values. The numbers found for K_1 and K_2 were 13.78 and 1.462 respectively. *F. B. K.*

Electromotive Forces

Contact electricity of metals. *J. Erskine-Murray. Proc. Roy. Soc.* **63,** *113 (1897); Phil. Mag.* [4] **45,** *398 (1898).* — The object of this research was to study and measure the variation of contact electricity of a pair of conductors, due to changes in the state of that portion of the surface of each conductor which is separated from the other conductor by an insulating medium. The method was the zero one of Lord Kelvin and all measurements were made against a standard gold plate. The potential difference increases with the degree to which the surface of the metal to be tested is polished. Thus a zinc plate that had been polished with glass-paper gave 0.7 volt; this difference rose to over one volt when the plate was burnished. Intermediate states of polish give intermediate values of potential. The production of thin films of oxids lowers the potential by amounts varying with the thickness of the film and approaching the value for oxid. This fact alone is enough to show that the values in Volta's fundamental experiment are not due to the presence of oxygen. The potential difference between dry lead and lead covered with water is about 0.9 volt.

The author has studied the effect of gases and of change of temperature. To eliminate the effect of air, a plate of copper was scratched under melted wax, the change being only about 0.1 volt. Sodium against gold gave 3.56 volts. These experiments showed that when two metals were coated with the same non-conductor, such as wax or glass, their potential was not sensibly different from that of the bare metals in air and that gaseous films played no essential part in the phenomena.

It is impossible to read this paper without coming to the conclusion that the author is observing and measuring a real phenomenon. Unfortunately the author does not point out the bearings of his work on the most recent hypotheses in regard to the voltaic cell. It is to be hoped that such a discussion is to form the basis for a second paper. The present state of things is intolerable,

one set of men trying to establish a certain point of view and another set trying to retain a conflicting hypothesis, each side scrupulously avoiding any reference to the experiments or arguments of the opposing group. *W. D. B.*

Contact electricity of metals. *Lord Kelvin. Phil. Mag.* [5] **46,** *82* (*1898*). — A discussion of Volta's fundamental experiment in which the effect of oxid and of moisture is considered. Special stress is laid upon the point of view that the Peltier heat is a measure of the change of the electromotive force with the temperature and is not a measure of the contact difference between metals. Unfortunately there is no discussion of the state of things when a cell is on closed circuit. Lord Kelvin takes time to ridicule the people who believe in the hypothesis of De la Rive; but he ignores Faraday completely. This one-sided way of looking at things is the more deplorable because the experiments of Erskine-Murray (preceding review) make it reasonably certain that the potential difference between metals is not zero. This apparent narrow-mindedness is not peculiar to Lord Kelvin nor to the Voltaists in general; the upholders of the chemical theory so-called are every bit as uncompromising in their refusal to look at the other side of the question. *W. D. B.*

Studies of decomposition voltages. *E. Bose. Zeit. Elektrochemie,* **5,** *153* (*1898*). — The best results are obtained when the potential difference is varied continuously and when the current is kept as low as possible. In most cases there was no actual break at the point where an ion separates, but this variation from the theoretical form is believed to be due to changes in the concentration at the surface of the electrode, since such a change would produce the effect noticed. The decomposition point is easy to determine when solids precipitate, but this ceases to be the case when a gas is given off. Solutions of copper salts show two characteristic decomposition points, the first being probably that at which Cu_2^{++} discharges and the second the one for Cu^{++}. From silver nitrate solutions silver separates only as Ag^{+}. The author has studied the behavior of a large number of acids and finds that, in general, there are as many decomposition points as there are anions derived from the acid plus two. Thus all the acids (and bases) have an anodic decomposition point at 1.08 volts (measured against the hydrogen electrode) at which the $\overline{\overline{O}}$ of the water separates and another at 1.67 volts where hydroxyl precipitates. In addition, nitric acid shows a point at 1.88 volts where $\overline{NO_3}$ separates and phosphoric acid two, one at 1.96 volts for $\overline{\overline{HPO_4}}$ and one at 2.18 volts for $\overline{H_2PO_4}$. The oxygen electrode depolarizes rapidly in the solution of a mercurous salt. *W. D. B.*

An experimental contribution to the osmotic theory. *W. Nernst and E. Bose. Zeit. Elektrochemie,* **5,** *233,* (*1898*). — According to the Nernst theory the potential difference between a metal and a solution depends upon the concentration of that metal as ion in the solution and not upon the concentrations of other substances. The authors have decreased the concentration of the electrode metal as ion electrolytically by means of a second circuit. A slowly dropping mercury electrode was measured in sulfuric acid against an electrode

consisting of mercury covered with mercurous sulfate. The secondary or electrolytic electrodes were of platinum. A potential difference of 0.443 volt was obtained, showing a concentration of mercury that must be multiplied by 10^{15} in order to equal the concentration of mercury as ion in a solution of the same sulfuric acid saturated with mercurous sulfate. This electrode polarized with extraordinary rapidity. With a silver electrode in hydrochloric acid measured against silver and silver chlorid the maximum potential difference obtained was 0.423 volt, corresponding to a concentration of silver as ion at the constant electrode 10^{7} times as great as at the other electrode. *W. D. B.*

The theory of the formation of amalgams of the alkalies. *A. Schoeller. Zeit. Elektrochemie*, **5**, *259* (*1898*).—Sodium and barium amalgams of different concentrations in sodium hydroxid and barium hydroxid solutions respectively were measured against the calomel electrode. The change of the electromotive force with the concentration was given very accurately by the formula for amalgam electrodes. This is very surprising because this is a case to which the formula does not apply, the heats of dilution not being zero.
W. D. B.

Contribution to the theory of the vapor-pressure of homogeneous mixtures. *F. Dolezalek. Zeit. phys. Chem.* **26**, *321* (*1898*).—With a view to confirming Nernst's formula connecting the E. M. F. of a reversible cell with the partial vapor-pressure of the dissolved substances the author makes a series of determinations of the vapor-pressure over hydrochloric acid solutions (30°) and also of the E. M. F. of the corresponding H-Cl-gas elements. The concentrations range from 4.98 to 12.25 normal. The results show good agreement with the theory. For the weaker solutions the dynamical method was employed, the difficulty of accurately measuring the large volume of indifferent gas being overcome by the happy idea of evolving hydrogen and oxygen from a small electrolytic cell and determining its loss in weight. The statical method was employed in the more concentrated solutions. The author might perhaps have spared himself some trouble by making use of Allan's determinations of vapor-pressure (**2**, 120). *F. B. K.*

Correction (**Electromotive force and distribution equilibrium**). *R. Luther. Zeit. phys. Chem.* **26**, *170* (*1898*).—An admission of Bucherer's point emphasized in the review (**1**, 521). The author adds that even with "purely aqueous" solutions the constancy of the E. M. F. of elements with the same solid phase is not necessary, because, as is the case of $CaCl_2 6H_2O$, two different solutions may be in equilibrium with the same hydrate. *F. B. K.*

A simple method of determining the polarization. *C. Heim. Zeit. Elektrochemie*, **4**, *527* (*1898*).—For an electrolytic cell we have the relation $p_1 = e + i.w$, where p_1 is the potential difference at the electrodes, e the electromotive force of polarization, w the resistance of the electrolyte, and i the strength of a constant current. If we separate the solution into two distinct parts by means of a third electrode, we shall have for the potential difference between the electrodes, the relation $p_2 = 2e + i.w$ on the assumption that the resistance of the third electrode is negligible. Subtracting the first equation from the second we have $e = p_2 - p_1$. The author describes his attempts to make an

apparatus in which the third electrode can be inserted and taken out easily and quickly and yet shall separate the two solutions absolutely when in place. He has not yet succeeded in devising an entirely satisfactory arrangement.

W. D. B.

Some lecture experiments. *F. W. Küster. Zeit. Elektrochemie*, **4**, *503 (1898).* — In the cell Cu | $Cu(OH_2)$ | KNO_3 | $Pb(NO_3)_2$ | Pb the current flows through the solutions from copper to lead. If the lead and lead nitrate be replaced by cadmium and cadmium sulfate, the copper becomes cathode. In the cell Cu | CuS | KNO_3 | $CdSO_4$ | Cd the cadmium is cathode, but copper becomes cathode if the cadmium and cadmium sulfate be replaced by zinc and zinc sulfate. Zinc can be made cathode by substituting potassium copper cyanid for the copper sulfid. It is shown how the Nernst theory applies in each case.

W. D. B.

Some forms of the most common galvanic cells. *E. Petersen. Zeit. Elektrochemie*, **5**, *261 (1898.)* — In the Bunsen cell replacing the nitric acid by potassium permanganate, hydrogen peroxid or lead peroxid was no improvement. A cell Zn | NaCl | $FeCl_3$ | C gives about 1.72 volts dropping to 0.54 volt when all the ferric chlorid is reduced to ferrous chlorid and iron precipitates on the cathode. Potassium ferricyanid may also be used instead of ferric chlorid.

W. D. B.

On the potential gradients at metallic electrodes during discharge by X-rays. *C. D. Child. Wied. Ann.* **65**, *152 (1898).* — The fall of potential from point to point in the air between two charged metallic plates, measured by a drop-electrode, may under ordinary circumstances be represented by a straight line. If, however, the air is made to conduct by X-rays the line becomes very much steeper near the electrodes, representing a rapid alteration of potential at the surfaces of the plates. The effect of varying the conditions, including the nature of the metal, was investigated. *F. B. K.*

The determination of low temperatures. *G. W. Meyer. Elektrochem. Zeit.* **5**, *6 (1898).* — The magnetic susceptibility of iron varies with the temperature and it is proposed to use the measure of this change as a measure of temperature difference. The two methods proposed are the direct determination of the magnetism and the measurement of the current induced by the change of magnetic induction. It is suggested that this might be valuable for low temperature determinations, but nothing is said as to the degree of accuracy to be obtained. *W. D. B.*

Electrolysis and Electrolytic Dissociation

The electrolysis of calcium chlorid solutions. *F. Oettel. Zeit. Elektrochemie*, **4**, *1 (1898).* — In consequence of the work of Bischoff and Foerster on the same subject (**2**, 456) the author publishes some experiments of his own made in 1894. By the electrolysis of calcium chlorid solutions at ordinary temperature the author obtained about a 70 percent yield of chlorate. At 70°–95° the yield runs up to 80 percent; at yet higher temperatures much hypochlorous acid is formed. It was hoped that adding potassium chlorid to precipitate potassium chlorate would increase the yield, but this was not the case. Instead

lime or calcium oxychlorid precipitated at the cathode. The exact reason for this was not discovered ; but the fact remains that when there are other salts in the solution a precipitate is formed at the cathode. Presence of copper oxid in the solution causes the hypochlorite to decompose with evolution of oxygen ; nickel oxid works in the same way ; ferric oxid is much less disturbing, and lead peroxid has even less effect.

The author considers that the formation of chlorate takes place according to two reactions : (1) the oxidation of hypochlorites ; (2) the direct combination of chlorin and oxygen at the anode. In neutral solutions the first is the main reaction ; in strongly alkaline the second, while both occur in slightly alkaline solutions. In the electrolysis of calcium chlorid solutions the first reaction is the more important. *W. D. B.*

Studies on the electrolysis of the alkali chlorids. *F. Winteler. Zeit. Elektrochemie*, **5,** *10, 49, 217 (1898).*—If a neutral potassium chlorid solution be electrolyzed between carbon electrodes there is always evolution of oxygen at the anode, decomposition of the carbon electrode and formation of hydrochloric acid, this last being due to the chlorin acting on the water. All of this can be prevented by adding hydrochloric acid to the solution ; but then the yield of caustic alkali decreases. Since perchlorates can easily be obtained by the electrolysis of chlorates, it became a question whether perchlorate might not be present as impurity in commercial chlorate ; but this proved not to be the case. Experiments on the electrolysis of potassium chlorate in neutral solution showed that this salt could easily be converted completely into perchlorate, the effective yield decreasing with rising temperature (Cf. **2,** 269). Starting with 20 and 50 percent solutions of sodium chlorate, experiments were made to determine the effect of current density. Satisfactory results were not obtained until a little free acid was added and the solutions stirred. The current yield is over 90 percent until the concentration of the undecomposed sodium chlorate drops below 10 percent provided the solution is kept cool. At the temperature of 100° there is more reduction than oxidation. *W. D. B.*

On the electrolysis of the alkali chlorids. *H. Wohlwill. Zeit. Elektrochemie*, **5,** *52 (1898).*—The author sums up his results as follows :

1. Hypochlorite is formed when the potential difference between the anode and a hydrogen electrode exceeds 1.2 volts. The reaction is almost quantitative when this potential difference does not exceed 1.3 volts and is probably to be described by the equation

$$\overline{Cl} + \overline{O}\,\overline{(++)} = \overline{ClO}.$$

2. An increased formation of hypochlorite takes place only when the potential difference exceeds 2.1 volts. It is due to a secondary chemical action of chlorin on the alkali.

3. Chlorate is formed by an ion reaction made possible through the addition of positive electricity. This reaction is, however, not the uniting of chlorin and hydroxyl as ions but is probably to be expressed by the equation

$$2\overline{ClO} + \overline{OH}\,\overline{(++)} = HClO_3 + \overline{Cl}.$$

The author has determined the potential-current or decomposition curves

for different mixtures of sodium hydroxid and sodium chlorid, finding many breaks. The paper furnishes an excellent example of the modern methods of attacking electrolytic problems, though it must be admitted that the decomposition curves were not of great assistance in the discussion. *W. D. B.*

Electrolytic reduction of paranitrotoluene to parahydrazotoluene. *K. Elbs. Zeit. Elektrochemie*, **4**, *499* (*1898*). — It is possible to use currents of 10–20 amp/qdm in the reduction of nitro compounds to azo substances and currents of 2–6 amp/qdm in the reduction of nitro compounds to hydrazo substances. In a lecture experiment the author reduced 10 g of *p*-nitrotoluene to *p*-hydrazotoluene in fifty minutes. The experiment with *p*-nitrotoluene is an especially good one because the hydrazotoluene is sparingly soluble and does not oxidize so readily in the air as do many of the hydrazo compounds. *W. D. B.*

On the electrolytic reduction of aromatic nitro compounds to azo and hydrazo substances. *K. Elbs and O. Kopp. Zeit. Elektrochemie*, **5**, *108* (*1898*). — Working with aqueous alcohol at the boiling-point and adding sodium acetate instead of sodium hydroxid, it is possible to use currents of 8–16 amp/qdm. The conditions are given for preparing azobenzene, hydrazobenzene, *o*-azotoluene, *p*-azotoluene, *p*-hydrazotoluene, *p*-azo-*o*-xylene, *p*-hydrazo-*o*-xylene, *m*-diamidoazobenzene, *m*-diamidohydrazobenzene, *m*-diamidobenzidin. In no case does the yield fall below 70 percent of that required by theory and in most instances it is much higher. *W. D. B.*

On the electrolytic reduction of *m*-nitro-*p*-toluidin. *K. Elbs and B. Schwarz. Zeit. Elektrochemie*, **5**, *113* (*1898*). — It is necessary to work with a current density not exceeding 4–5 amp/qdm, otherwise much *m*-toluylenediamin is formed. The *m*-diamido-*o*-azotoluene thus formed appears to melt at 145°, 132°, 158° and intermediate temperatures. The probability is that the authors were struggling rather unsuccessfully with a substance having two liquid modifications. *W. D. B.*

On the electrolytic indigo vat. *A. Binz. Zeit. Elektrochemie*, **5**, *5* (*1898*). — Indigo blue is ordinarily reduced to indigo white by zinc dust in alkaline solution. When it is attempted to carry out the operation electrolytically, it is found that the reduction is very incomplete. The author discovered that in the ordinary process there seems to be no relation between the amount of alkali and the amount of indigo reduced. He concluded therefore that the zinc acted directly on the indigo. To test this he placed the anode in one beaker and the cathode in another. The main reduction took place at the anode. With low concentrations of alkali there is very little reduction, presumably because of the formation of hydroxid on the electrode. With increasing concentration of alkali the local reduction first increases and then decreases. *W. D. B.*

The reduction of indigo by electrolytically precipitated zinc. *A. Binz. Zeit. Elektrochemie*, **5**, *103* (*1898*). — To test quantitatively the difference in reducing power between zinc and hydrogen, the author passes the current through two cells arranged in series. In both the cathode consisted of a copper netting filling almost the entire vessel. The cathode solution consisted of in-

digo and sodium zincate in the first cell and of indigo and sodium hydroxid in the second. In the first cell no zinc precipitated on the cathode and the reduction was roughly fifteen times as much as in the sodium hydroxid solution. While the indigo is reduced quantitatively to indigotin, the yield is not quantitative because the indigotin is decomposed to a certain extent. This part of the reaction was not studied farther. *W. D. B.*

The electrolytic formation of nitrobenzene from orthonitrobenzoic acid. *C. Schall and R. Klien. Zeit. Elektrochemie*, **5**, *256 (1898)*. — It is stated that traces of nitrobenzene are formed by the electrolysis of the sodium salt of *o*-nitrobenzoic acid when dissolved in the free acid. The result was not very satisfactory since other decompositions took place. *W. D. B.*

On successive reductions of nitrobenzene under definite potential differences. *F. Haber. Zeit. Elektrochemie*, **4**, *506 (1898)*. — The author considers that oxidation and reduction processes depend chiefly on the potential difference between the solution and the electrode at which the reaction takes place. A platinum electrode in a solution consisting of 25 g nitrobenzene, 40 g sodium hydroxid, 50 g water and 350 g alcohol gave a value of 0.72 volt against a decinormal calomel electrode. If polarized until bubbles of hydrogen appeared the value rose to 1.29 volts. In the first experiment the current density was regulated so that the potential difference between the platinum electrode and the decinormal calomel electrode never exceeded 0.93 volt. The reaction products consisted almost exclusively of azoxybenzene, only traces of azobenzene, hydrazobenzene and anilin being present. Special experiments showed that the anilin was not formed by reduction of the hydrazobenzene. It appears that the primary reduction product is nitrosobenzene, C_6H_5NO, then β-phenylhydroxylamin. For the most part these two react, as observed by Bamberger, forming azoxybenzene; a small portion of the β-phenylhydroxylamin is however reduced to anilin. The hydrazobenzene comes from the partial reduction of the azoxybenzene, while the cause for the appearance of the azobenzene has not been worked out.

In acid solutions the main products are azoxybenzene, *p*-amidophenol, *p*-phenetidin, benzidin and anilin. The first two stages are the same as in the alkaline reduction, nitrosobenzene and then phenylhydroxylamin. The two substances do not react rapidly in acid solution and therefore there is not so much azoxybenzene formed as in alkaline solutions. On the other hand in acid solutions β-phenylhydroxylamin changes readily to *p*-amidophenol and to *p*-phenetidin, while the hydrazobenzene formed from the azoxybenzene changes to benzidin. To show the formation of β-phenylhydroxylamin the author reduced nitrobenzene in aqueous acetic acid, with a high current density.
W. D. B.

Electrolytic preparation of a new dithiodisulfid and of some dithiodisulfids. *C. Schall and S. Kraszler. Zeit. Elektrochemie*, **5**, *225 (1898)*. — By electrolysis of substances having the general formula (RCS)SM the metal precipitates and there is formed the disulfid (RCS)S.S(SCR). Starting with the diethyl ammonium salt of diethyldithiocarbaminic acid the authors have isolated the tetrethylthiuramdisulfid $[(C_2H_5)_2N.CS]S.S[SC.N(C_2H_5)_2]$ previously obtained

in another way by Grodzki. Starting with $C_2H_5S.CSSK$ they have obtained the new substance $(C_2H_5SC)S.S(CSC_2H_5)$. *W. D. B.*

Electrolytic preparation of β-phenylhydroxylamin. *F. Haber. Zeit. Elektrochemie*, **5**, *77 (1898)*. — The cathode is a spiral platinum tube which can be kept cool by passing water through it; the anode is platinum foil. The anode solution is sulfuric acid and is placed in a porous cell. The cathode solution consists of 50 g nitrobenzene and 430 cc acetic acid diluted with water to 850 cc. The current density at the anode was 0.04 amp/qdm and the temperature was not allowed to rise above 20°. The cathode solution was treated with ether and water, neutralized with magnesia, evaporated and dissolved in petroleum ether from which the β-phenylhydroxylamin then crystallizes. The yield is less than one gram. *W. D. B.*

On the electrolysis of zinc chlorid solutions and on the nature of zinc mud. *F. Foerster and O. Günther. Zeit. Elektrochemie*, **5**, *16 (1898)*. — There is no difficulty in precipitating zinc electrolytically in any desired amount from zinc chlorid solution provided the solution be kept slightly acid. The authors recommend doing this by means of a secondary circuit setting free chlorin. Working with basic zinc chlorid solutions the authors obtained a precipitation of zinc corresponding well with that required by Faraday's law. Ashcroft is said to have obtained results fifty percent in excess of the theoretical, but this cannot be tested because the conditions under which he worked are not known. In the second half of the paper the authors discuss their theory in regard to the formation of zinc mud. Their idea is that it is formed only when, in addition to zinc, hydrogen is evolved in such quantities that zinc hydroxid, basic zinc chlorid or basic zinc sulfate precipitates at the cathode. The presence of these salts prevents the formation of a coherent, crystalline mass of zinc. There is also a discussion of the effect due to the presence of different oxidizing agents at the cathode. *W. D. B.*

The hydrogen voltameter and its trustworthiness. *H. A. Naber. Elektrochem. Zeit.* **5**, *45 (1898)*. — It is claimed that, with the author's improved hydrogen voltameter, there is no difficulty in measuring quantities of electricity with an error not exceeding one-twentieth of one percent. *W. D. B.*

Some applications of the electric arc. *G. Bredig. Zeit. Elektrochemie*, **4**, *514 (1898)*. — When sparks from an oscillator pass through petroleum, the latter is decomposed. This is to be taken as analogous to the behavior in Deville's hot-cold tube. With the electric arc under petroleum some acetylene is formed. Attention is called to the fact that when an arc is formed under pure water between metallic poles, the metallic vapors are suddenly cooled by the water producing finely divided particles of metals suspended in the liquid. *W. D. B.*

On the decomposition of sulfur by electrolysis. *T. Gross. Elektrochem. Zeit.* **5**, *48 (1898)*. — By the electrolysis of a fused mixture of silver chlorid and silver sulfate the author has prepared more "bythium" (**1**, 620). Even now no attempt has been made to prepare bythium in quantity. The chlorid is said to be white, infusible and insoluble in acids and in ammonia. A new barium com-

pound has also been discussed and a hitherto unknown white vapor. Neither of these substances have been studied (See **2**, 140). *W. D. B.*

Purification and decolorizing of sugar solutions by ozone, by electrolysis and by both simultaneously. *F. Peters. Zeit. Elektrochemie*, **5**, *265* (*1898*). — It was found that syrups were purified very much more effectively by the simultaneous action of ozone and of electrolysis than by either method taken singly. *W. D. B.*

A quantitative electrolytic method for the separation of the halogens, chlorin, bromin, iodin. *H. Specketer. Zeit. Elektrochemie*, **4**, *539* (*1898*). — To determine iodids in the presence of bromids and chlorids, the author electrolyzes with a silver anode and platinum cathode under a potential difference of 0.13 volt until the iodin has been completely converted into silver iodid, this salt being then weighed without removing it from the electrode. To determine bromids in presence of chlorids the same process is repeated under a potential difference of 0.35 volt. *W. D. B.*

A method of separating cobalt and nickel. *A. Coehn. Zeit. Elektrochemie*, **4**, *501* (*1898*). — When a solution containing salts of cobalt and nickel is electrolyzed, cobalt peroxid is precipitated at the anode entirely free from nickel. This can also be used qualitatively as a test for the presence of cobalt. *W. D. B.*

Two electrolytic methods of determining zinc. *H. Paweck. Zeit. Elektrochemie*, **5**, *221* (*1898*). — An amalgamated brass netting serves as cathode and the electrolyte may contain sulfuric acid and sodium sulfate in addition to the zinc salt or sodium hydroxid and Seignette salt. Either method gives satisfactory results. *W. D. B.*

On the electrical conductivity of potassium nitrate. *J. C. H. Kramers. Arch. néerl.* (*2*) **1**, *455* (*1898*). — The author has determined the conductivity of all possible mixtures of water and potassium nitrate over a range of temperature running up to 370° in the extreme case of the anhydrous salt. The specific conductivities at constant temperature vary with the concentration, passing through a maximum value. The concentration at which this maximum occurs (53 ± 1 g KNO_3 per 100 g solution) appears to be practically independent of the temperature. The curve obtained by plotting specific conductivities against concentrations is parabolic in form. *W. D. B.*

On electrolytic conduction in rarefied gases. *E. Wiedemann and G. S. Schmidt. Wied. Ann.* **61**, *737* (*1897*). — A current from 1000 storage cells was passed through a tube so arranged that the decomposition-products of the contained gas could be pumped away separately from near the two electrodes and quantitatively estimated. Hydrochloric acid and the haloid salts of mercury were treated in this way and in all cases the amount of free halogen found to be less than that calculated on the assumption of Faraday's law. *F. B. K.*

On the constitution of mercury. *C. Liebenow. Zeit. Elektrochemie*, **4**, *515* (*1898*). — The conductivity of liquid mercury changes only 0.1 percent per

degree while solid mercury and most pure metals show a change in the conductivity of about 0.4 percent per degree. Many alloys have as low a temperature coefficient as liquid mercury, and it is therefore concluded that this latter is a mixture of monatomic and polyatomic mercury. This assumption is said to be supported by the fact that addition of traces of other metals to mercury increases the conductivity. *W. D. B.*

The general validity of the law of dilution. *J. J. van Laar. Zeit. phys. Chem.* **25,** *79 (1898).* — The author is convinced of the validity of Ostwald's law of dilution in electrolytes and consequently that conductivity measurements give false values for the degree of dissociation α. In support of this view he shows that his formula for the heat of solution based on the theoretical dilution law yields results in closer agreement with the experimental numbers than when the formula is arranged to suit Rudolphi's empirical relation. He accounts for the anomalies in the conductivity determinations of α by the alteration of the dissociation constant K owing to the rise in temperature caused by heat developed in the passage of the current, and under this assumption, deduces the Rudolphi–van 't Hoff relation :

$$\frac{(\alpha c)^2}{(1-\alpha)c} = K.$$

The constant K however contains the difference of potential between the electrodes and it would be surprising, if such a dependence of the potential difference actually exists, that it should have escaped observation.

"The heat capacity of the solvent being greater than that of the single salt molecules and ions, the elevation of temperature of the latter will be much greater than that of the aqueous environment ... consequently the temperature of the salt molecules and ions will reach a very high value". The ions are indeed long-suffering. *F. B. K.*

On hydrolytic and electrolytic dissociation. *G. Platner. Elektrochem. Zeit.* **5,** *23 (1898).* — It is shown that the formation of cuprous hydrid by the action of hypophosphoric acid on copper salts is intelligible provided we assume that the acid takes oxygen from cuprous hydroxid. Since metallic silver is not formed by the action of hypophosphoric acid on potassium silver cyanid solution, the author concludes that silver hydroxid does not exist in the solution. After citing a few more cases in which hydrolytic decomposition has or has not taken place (Cf. **2,** 402), the author proceeds to show the advantages of hydrolytic dissociation over the hypothesis of electrolytic dissociation. Unfortunately he does not explain how hydrolytic dissociation accounts for the freezing-points and boiling-points of potassium hydroxid solutions. *W. D. B.*

The action of solutions on the sense of taste. *L. Kahlenberg. Bull. Univ. Wisconsin,* **2,** *1 (1898).* — Hydrogen as ion has a sour taste becoming astringent in dilute solutions. Hydroxyl as ion has an alkaline [or soapy] taste. Chlorin, bromin and iodin as ions have a salty taste, that of iodin being the least intense. The taste of NO_3 as ion is slight, somewhat salty, producing a burning sensation in concentrated solutions. Sodium, lithium, SO_4 and CH_3COO as ions are almost tasteless; potassium, magnesium, calcium and ammonium as ions have a bitter taste. Silver and mercury as ions have a dis-

tinctly 'metallic' taste. Silver as ion can be detected in $n/5000$ solution; mercury as ion in $n/2000$ solution; hydrogen as ion in $n/800$ solution; hydroxyl as ion in $n/400$ solution. The taste of the other ions can be recognized readily only in very much more concentrated solutions, $n/5$ to $n/25$. Acetic acid gives a much sourer taste than one would expect from the dissociation.

An investigation of some organic substances showed that the intensity stood in a qualitative relation to the readiness with which these substances permeate plant and animal membranes. Colloidal substances are tasteless. Alkaloids have a very bitter taste and it has been shown by others that these substances permeate protoplasm readily and exert a strong physiological effect on the nerves. In regard to acetic acid the reviewer would suggest that Walden's measurements on diffusion through semipermeable membranes showed that in some way the presence of hydrogen as ion causes other substances to pass that otherwise did not. It would thus be possible to get the taste of the undissociated acid. *W. D. B.*

Electric furnace for all styles of heating. *W. Borchers. Zeit. Elektrochemie*, **4**, *523* (*1898*). — A description of a furnace with detachable parts so that it can be used in various ways. *W. D. B.*

Dielectricity and Optics

On the absorption of short electrical waves by water. *P. Drude. Wied. Ann.* **65**, *499* (*1898*). — Electrical waves from a Righi exciter were sent through layers of water of varying thickness and the unabsorbed energy measured by a coherer. The author sums up his results as follows: (1) Water shows an increasing electrical absorption for decreasing wave-length λ, which is noticeable even in the neighborhood of $\lambda = 10$ cm; (2) In the use of Herz–Righi exciters the wave-length may be conditioned very materially by neighboring wave-lengths, whereby the results may, in some cases, be strongly influenced. *F. B. K.*

On the absorption of ultra-red rays in doubly refracting crystals. *J. Königsberger. Wied. Ann.* **61**, *687* (*1897*). — The absorption of ultra-red light of varying wave-length by a number of crystals in directions parallel to the optical axes was determined bolometrically and represented in the form of curves. The absorption curve for the isomorphic substances baryta and celestine are similar in shape and the minimum points occur for roughly the same wave-lengths. It is also noticed that the absorption caused by the presence of slight admixtures is quantitatively different in the different directions. *F. B. K.*

On the serial-spectra of the elements oxygen, sulfur and selenium. *C. Runge and F. Paschen. Wied. Ann.* **61**, *642* (*1897*). — An investigation of the "serial-spectra" (the compound line spectra of Schuster) of the above elements. The serial-spectra of sulfur and selenium are obtained by heating sulfuric and selenic acids respectively in an atmosphere of oxygen. The oxygen is evolved electrolytically in the spectrum tube itself. The general result of the investigation is that oxygen, sulfur and selenium possess analogous serial-spectra, each consisting of three series of triplets and probably a similar set of series of trip-

lets and probably a similar set of series of single lines or waves. The authors say "It is remarkable that these more or less intense spectral lines have remained hitherto unknown, and it appears to us therefore not impossible that many of the lines of unknown origin observed in the sun and stars may be attributed to known elements, if the latter are brought into incandescence under different conditions". *F. B. K.*

The photochemical action of turpentine. *J. Sperber. Chem. Zeit.* **22,** *No. 90 (1898).* — To test the hypothesis that the action of turpentine on photographic plates is due to rays emitted from the oil and not to the action of the vapor, the author made two experiments. In both, the plates were exposed to turpentine vapor; but in the first experiment rays from the liquid turpentine could strike the plates directly or by reflection while this was prevented in the second experiment. Complete reduction occurred in the first experiment while, in the second, there was reduction only at the edges of the plates, which had not been perfectly protected. The effect is therefore due to radiation from the liquid turpentine and the vapor of turpentine does not emit these rays to a measurable extent under the conditions of the experiment. *W. D. B.*

Crystallography, Capillarity and Viscosity

On the internal friction of electrolytic solutions. *H. Euler. Zeit. phys. Chem.* **25,** *536 (1898).* — Extending Arrhenius's exponential formula for internal friction in solutions of mixed salts to the ions and undissociated molecules of electrolytes the author obtains the following formula:

$$H = S^x A^y K^y$$

or, for normal solutions,

$$H = S^{(1-\alpha)} A^\alpha K^\alpha.$$

[H = internal friction, S, A, K are friction constants for the undissociated molecule, anion and cation respectively, x and y the corresponding concentrations and α the degree of dissociation.]

With the help of this formula and the results of Wagner's measurements of viscosity the friction coefficients of a number of ions are calculated. The numbers calculated from various salts for the same ion show fair agreement. A simple relation between the viscosity coefficients and the rates of migration of the ions is shown to hold approximately, except in the case of H and OH which form notable exceptions. The paper closes with a discussion of "negative friction". *F. B. K.*

Determination of the specific cohesion of copper, iron, nickel and cobalt. *R. Herzfeld. Wied. Ann.* **62,** *450 (1897).* — The author finds from the form of the solidified globules that the specific cohesion of the above metals is three times that of mercury. *F. B. K.*

ON THE DEMONSTRATION OF THE PHASE RULE[1]

BY PAUL SAUREL

If the energy, entropy, volume, temperature, pressure, and masses of the components of a phase be denoted by ϵ, η, v, t, p, m_1, m_2, ..., m_n, it can be shown that

$$d\epsilon = td\eta - pdv + \mu_1 dm_1 + \mu_2 dm_2 + \ldots + \mu_n dm_n.$$

If it be admitted that ϵ is a function of the independent variables η, v, m_1, m_2, ..., m_n, it follows that t, $-p$, μ_1, μ_2, ..., μ_n are the first derivatives of ϵ. Moreover, ϵ is a homogeneous function of the first degree of η, v, m_1, m_2, ..., m_n; for, when the entropy, volume, and masses are increased k-fold, the energy is also increased k-fold. Accordingly, by Euler's theorem,

$$\epsilon = t\eta - pv + \mu_1 m_1 + \mu_2 m_2 + \ldots + \mu_n m_n.$$

The comparison of these two equations yields the equation:

$$0 = \eta dt - vdp + m_1 d\mu_1 + m_2 d\mu_2 + \ldots + m_n d\mu_n;$$

and from this equation Gibbs[2] concludes that there exists an integral relation between p, t, μ_1, μ_2, ..., μ_n. This conclusion is unwarranted; but it is nevertheless correct, as may be shown by the following reasoning. ϵ is a homogeneous function of the first degree of η, v, m_1, m_2, ..., m_n; its derivatives, t, $-p$, μ_1, μ_2, ..., μ_n, are therefore homogeneous functions of the degree zero, that is to say they are functions of the ratios $\frac{\eta}{v}$, $\frac{m_1}{v}$, $\frac{m_2}{v}$, ..., $\frac{m_n}{v}$. If, then, from the $n+2$ equations which define t, $-p$, μ_1, μ_2, ..., μ_n in terms of η, v, m_1, m_2, ..., m_n, we eliminate the $n+1$ ratios $\frac{\eta}{v}$, $\frac{m_1}{v}$, $\frac{m_2}{v}$, ..., $\frac{m_n}{v}$, we shall find an integral rela-

[1] This note has already appeared, in part, in the *Procès-verbaux des Séances de la Société des Sciences de Bordeaux*.

[2] Gibbs. On the Equilibrium of Homogeneous Substances, p. 143.

tion between p, t, μ_1, μ_2, ..., μ_n. The existence of this relation is an essential point in Gibbs's demonstration of the phase rule. The existence of the relation between p, t, μ_1, μ_2, ..., μ_n can also be established by means of the following theorem:

If X_1, X_2, ..., X_n are the first derivatives of a function F of the independent variables x_1, x_2, ..., x_n, so that

$$dF = X_1 dx_1 + X_2 dx_2 + \cdots + X_n dx_n;$$

and if, further, F be such that

$$F = X_1 x_1 + X_2 x_2 + \cdots + X_n x_n,$$

then the functions X_1, X_2, ..., X_n are not independent, but are connected by an integral equation.

For, the comparison of the two above equations yields the third:

$$x_1 dX_1 + x_2 dX_2 + \cdots + x_n dX_n = 0;$$

or, as it may be written:

$$\begin{aligned}
&\left[x_1 \frac{\partial X_1}{\partial x_1} + x_2 \frac{\partial X_2}{\partial x_1} + \cdots + x_n \frac{\partial X_n}{\partial x_1}\right] dx_1 \\
+ &\left[x_1 \frac{\partial X_1}{\partial x_2} + x_2 \frac{\partial X_2}{\partial x_2} + \cdots + x_n \frac{\partial X_n}{\partial x_2}\right] dx_2 \\
&\quad \vdots \qquad\quad \vdots \qquad\qquad \vdots \\
+ &\left[x_1 \frac{\partial X_1}{\partial x_n} + x_2 \frac{\partial X_2}{\partial x_n} + \cdots + x_n \frac{\partial X_n}{\partial x_n}\right] dx_n = 0.
\end{aligned}$$

As the differentials dx_1, dx_2, ..., dx_n are independent, this equation requires that the coefficients of these differentials should be equal to zero; and the elimination of x_1, x_2, ..., x_n from the n resulting equations yields:

$$\begin{vmatrix}
\frac{\partial X_1}{\partial x_1}, & \frac{\partial X_2}{\partial x_1}, & \cdots, & \frac{\partial X_n}{\partial x_1} \\
\frac{\partial X_1}{\partial x_2}, & \frac{\partial X_2}{\partial x_2}, & \cdots, & \frac{\partial X_n}{\partial x_2} \\
\vdots & \vdots & & \vdots \\
\frac{\partial X_1}{\partial x_n}, & \frac{\partial X_2}{\partial x_n}, & \cdots, & \frac{\partial X_n}{\partial x_n}
\end{vmatrix} = 0.$$

The vanishing of the Jacobian of $X_1, X_2, \ldots, X_n$ shows that these functions are not independent but are connected by an integral equation.

The application of this theorem to the functions $t, -p, \mu_1, \mu_2, \ldots, \mu_n$ which satisfy the equations:

$$d\epsilon = td\eta - pdv + \mu_1 dm_1 + \mu_2 dm_2 + \cdots + \mu_n dm_n,$$
$$\epsilon = t\eta - pv + \mu_1 m_1 + \mu_2 m_2 + \cdots + \mu_n m_n$$

is evident.

Université de Bordeaux

DISSOCIATION STUDIES, I

BY WILDER D. BANCROFT

In an unfinished series of papers on the equilibria of stereoisomers[1] there has been given a discussion of some of the phenomena to be expected when one substance changes more or less completely into another in the liquid phase at a moderately low rate of speed. In this paper it is proposed to outline some of the phenomena to be expected when one substance changes slowly into two different substances in the liquid or vapor phase; it is proposed to study the dissociation of compounds from the point of view of Duhem's theory. The paper is also a continuation of a preceding one on the pressure-temperature diagrams for two-component systems.[2] In Fig. 1 is given the schematic

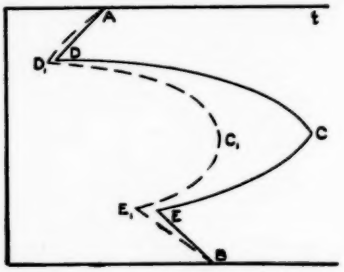


Fig. 1

concentration temperature diagram for a binary system in which a compound exists that does not dissociate measurably into the components in solution. Such a system could be realized with acetic anhydrid and water, since acetic anhydrid must freeze at some temperature, and it is very improbable that acetic acid and acetic anhydrid form two liquid layers at any temperature.

[1] Jour. Phys. Chem. **2**, 143, 245 (1898).

[2] Ibid. **3**, 1 (1899).

In the diagram, Fig. 1, the point A represents the melting-point of the component A, the point B the melting-point of the component B, and the point C the melting-point of the compound C. The curve AD is the boundary curve for component A, solution and vapor, DCE is the boundary curve for compound, solution and vapor, while EB is the corresponding curve for the component B, solution and vapor. If the compound does not dissociate at all, DC and EC are two curves meeting at an angle;[1] otherwise the curve has a true, rounded temperature maximum. The diagram has been so drawn that the compound melts at a higher temperature than either of the components. It is not known whether this is necessarily the case; but it is certainly the most common state of things. It is to be noticed that the concentrations, as shown in the diagram, are the analytical concentrations and that the amount of the compound present in the solution is not given.

If the compound be supposed to dissociate in solution, the dissociation products will lower the partial pressure of the compound and will therefore lower its freezing-point. Since the amount of dissociation is fixed for each temperature, provided the vapor phase be infinitesimal or constant in amount, the freezing-point will be lowered only to a perfectly definite amount. There will thus be a stable melting-point corresponding to the stable triple-point in the case of stereoisomers. In the diagram, Fig. 1, this point is marked C_1. Other things being equal, the temperature difference between C and C_1 will vary with the amount of dissociation. If the compound be sufficiently dissociated, the point C_1 may fall below the continuation of BE, in which case a stable melting-point is no longer possible. If the point C_1 be lowered still farther, the whole curve now marked DCE may lie below the extension of the curves AD and BE, in which case the compound cannot exist in equilibrium with solution. This is apparently the case with the double salt,[2]

[1] Cf. van der Waals. Kon. Akad. Wetensch. Verslag, Amsterdam, **1897**, 385.

[2] Bauer. Zeit. phys. Chem. **18**, 180 (1895).

$HgI_2 2AgI$, and with the racemate form of methyl mannosid.[1]

If the rate of dissociation in solution be sufficiently low, the compound may be made to melt at any temperature between C and C_1, the highest temperature being reached by rapid heating. If we start with mixtures containing the compound and an excess of one of the components, we shall get melting-points lying on the curve DCE if we heat rapidly and melting-points lying on a curve passing through C_1 in case we heat very slowly. Theoretically this new curve will cut a new curve AD_1 at D_1 at a temperature lower than that of D_1 and will cut a new curve BE_1 at E_1 at a temperature lower than that of E_1. It is probable however that, in the large majority of cases, no serious error will be introduced by assuming that the same curves AD and BE are obtained whether we heat slowly or rapidly and that D_1 coincides with D and E_1 with E. We should then have the curve DC_1E for the stable freezing-point curve and DCE as the limiting instable freezing-point curve, while solid, liquid and vapor can be realized temporarily in any part of the field CDC_1EC provided of course that the curve DCE can be realized experimentally.

From the published data phthalic anhydrid and water appeared to be a system coming under this head. Phthalic acid is said by Lossen[2] to melt at 184°; by Ador[3] to melt at 203° when pulverized, and at 213° when in large crystals. Graebe[4] says that when not heated too rapidly the melting-point is 190°-195°. Howe[5] appears to have been misled by these discrepancies into assuming the existence of two isomeric forms of phthalic acid, one melting at 184° and the other at 203° or higher. This error has been corrected by Wheeler[6] who attributes the variation of the melting-point, as Remsen[7] had

[1] Fischer and Beensch. Ber. chem. Ges. Berlin, **29**, 2927 (1897).
[2] Liebig's Annalen, **144**, 78 (1867).
[3] Ibid. **164**, 230 (1872).
[4] Ibid. **238**, 321 (1887).
[5] Am. Chem. Jour. **18**, 390 (1896).
[6] Ibid. **18**, 828 (1896).
[7] Ibid. **3**, 30 (1881).

done before him, to the formation of anhydrid and water. Wheeler, however, practically denies the existence of any point at about 184°. He says: "It is well-known that the melting-point of orthophthalic acid is really its decomposition point, i. e. the acid loses water and passes into the anhydride, the melting-point of the anhydride being about 128°. It would be expected that this decomposition might be produced at different temperatures according to the length of time the substance is heated, according to the quantity of the substance taken and according to the condition, both physical and chemical, of the sample. Such indeed has been found the case. It is therefore not surprising that, if phthalic acid is heated above 128°, different melting-points are obtained under different conditions." This statement is not in accord with the theory as developed in these pages. The discrepancy is due to the fact that Wheeler is discussing the changes that occur during continuous distillation from an open melting-point tube, for he says explicitly that "the acid loses water". At the end of the experiment Wheeler has only phthalic anhydrid and no phthalic acid. Barring the overlooking of a possible eutectic point with phthalic acid and phthalic anhydrid as solid phases,[1] this statement of Wheeler's is entirely correct; but it applies only to a case of fractional distillation and therefore throws no light on the question of a stable melting-point for phthalic acid. It occurred to me that the melting-point of 184° obtained by Howe was probably the stable melting-point of phthalic acid, corresponding to the point C_1 in the diagram. At my request Mr. O. W. Brown made some measurements in sealed tubes, completely immersed in a sulfuric acid bath. In order to prevent explosions the walls of the tube were fairly thick. It was therefore not possible to heat as rapidly as might have been desired and the highest melting-point reached was 198° instead of 203° and over. On long heating the melting-point dropped to 184°, but could not be forced lower. Although heated for several hours at 182°–183°,

[1] As a matter of fact, no such eutectic point occurs; but there is nothing in Wheeler's published work to show this.

it remained perfectly solid, melting sharply at 184°. This temperature is therefore the stable melting-point of phthalic acid corresponding to the point C_1 of the diagram. Fifty reacting weights of the anhydrid and 33.3 reacting weights of water melted completely at 190° on rapid heating and at 182° on slow heating. When 4.8 reacting weights of water were added to fifty of anhydrid the two temperatures were 173° and 156°; with one of water 142° and 135°; with 0.41 reacting weight of water 136° and 130°; with no water 128°. Owing to the thermometer being outside and not inside the sealed tubes, these determinations are necessarily not very accurate. The most striking feature about these results is that the plotted curves end at the melting-point of phthalic anhydrid and not at a eutectic point. The only possible interpretation of this is that phthalic anhydrid and phthalic acid crystallize together to form a series of solid solutions. It will be shown later in this paper that this hypothesis[1] enables us to explain some experimental results obtained by Ramsay and Young that would otherwise be quite unintelligible.

This formation of solid solutions takes the system, phthalic anhydrid and water, out of the class of two components and a dissociating compound; but the theory can be applied to this case in exactly the same way as has been done. The only change to be made in Fig. 1 is to replace CDA by a curve CA and C_1D_1A by a curve C_1A.

If the curve for rapid heating ran up to the true melting-point of phthalic acid, 213°, if pure phthalic acid separated from solution and if the curve were symmetrical on both sides of the upper melting-point, it would be a simple matter to calculate the dissociation of phthalic acid at 184° by determining the concentrations on the curve DCE corresponding to a temperature of 184°. The first condition was not fulfilled in the experiments of Mr. Brown and the second is not fulfilled at all, so that for the present we are unable to estimate the amount of dissociation

[1] This hypothesis is now being tested experimentally by Mr. M. R. Ebersole.

of phthalic acid at 184°. An experiment was made by Mr. Brown to determine whether phthalic anhydrid dissolves as such in water at ordinary temperatures. The reason for supposing that this might be possible is that metaphosphoric acid dissolves as such in water and then slowly takes up water, forming orthophosphoric acid.[1] It was found, however, that the titre of the solutions did not vary with the time, so that there is either no dissociation in dilute aqueous solutions or the equilibrium is reached with great rapidity. Of the two the first hypothesis is the more probable. As yet no titrations have been made at high temperatures.

As systems will undoubtedly be found in which it will be possible to determine the dissociation of the compound by direct experiment,[2] it will be well to supplement the discussion of Fig. 1 by a brief consideration of the triangular diagram for such a case.

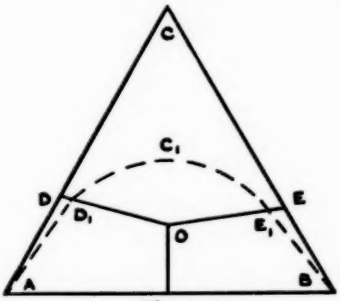


Fig. 2

As in Fig. 1, A, B and C denote the melting-points of the components A and B and of compound C respectively. The lines ADC and CEB represent the state of things when the compound does not dissociate at all and the only solutions consist of the compound plus one or the other of the components.

[1] Sabatier. Ann. Chim. Phys. (6) **18**, 409 (1887).

[2] In the system, amylene and acid, there is no difficulty in determining the amount of dissociation at 100°, but the dissociation is presumably so slight at the temperatures at which solid phases appear, as to make this system uninteresting, especially in view of the experimental difficulties that would be involved in a complete investigation.

If the three substances can be taken in any desired proportions, the boundary curves for the system will be represented by the curves DO, EO and FO, O being the quintuple point at which A, B and C are in equilibrium as solids with solution and vapor. Such a point could be realized at very low temperatures with acetone, chloroform, and acetonechloroform since the compound is not formed directly from the components nor does it dissociate into the components.[1] If there is reversible equilibrium between the components and the compound the boundary curves change into $AD_1C_1E_1B$, the component A being solid phase along AD_1, the compound along D_1C_1E and the component B along E_1B. The point C_1 is the stable melting-point of the compound and D_1C_1E is a continuous curve. Since ADCEB are the limiting concentrations for rapid heating and $AD_1C_1E_1B_1$ are the concentrations reached after long heating, the fields between these two sets of curves represent the concentrations passed through as the freezing-points vary. From the triangular diagram it is apparent that D_1 can coincide with D and E_1 with E only when there is no dissociation at the temperatures connoted by those points. From the theorem of van Rijn van Alkemade we know that the temperature of D_1 must be lower than that of D and the temperature of E_1 lower than that of E.

In considering the equilibria of stereoisomers it was shown that if the equilibrium in the system, liquid and vapor, were displaced by change of temperature, the freezing-point obtained by sudden cooling would differ from the stable freezing-point. The same thing will of course occur in the case of a dissociating compound. In the case of phthalic acid the dissociation must increase with rising temperature and therefore, on heating the solution, say to 220° and cooling suddenly, the solution should begin to freeze at temperatures below 184°, provided always the cooling can be effected more rapidly than the readjustment of the equilibrium. Working as Mr. Brown did with small tubes and the thermometer in the bath, it was of course impossible to distinguish such a phenomenon from a case of supercooling so this

[1] Cameron and Holly. Jour. Phys. Chem. **2**, 322 (1898).

part of the theory was not verified experimentally. It should be kept in mind that the rate at which the freezing-point of the crystals falls from 203° or 198° to 184° is no measure of the rate at which equilibrium is reached in the liquid itself. It is conceivable that the first change might take place relatively slowly and the second relatively rapidly. At some future date an attempt will be made to determine whether the apparent freezing-point of phthalic acid is affected measurably by changes in the initial temperature of heating.

From a study of the pressure-temperature diagrams we can deduce a number of interesting conclusions, some of which have already been tested experimentally. The case in which there is no dissociation either in the liquid or the vapor phase is shown in Fig. 3. To avoid confusion only the partial pressure curves are given, omitting those for the univariant systems in which

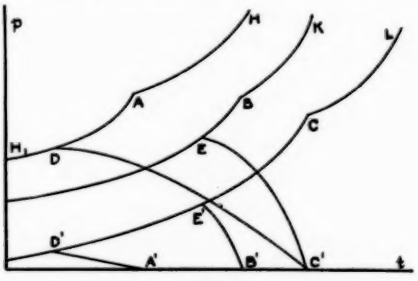


Fig. 3

there is no vapor phase.[1] H_1DA is the sublimation curve for pure A; AH the vaporization curve for pure A; K_1EB and BK are the corresponding curves for pure B; $L_1D'E'C$ and CL the same curves for the pure compound C. The temperature of the eutectic point with A and C as solid phases is that of the points D and D', while the temperature of the eutectic point with B and C as solid phases is that of the points E and E'. As the system passes along the boundary curve from the melting-point of A to the first eutectic point the variation of the partial

[1] The letter K_1 has been omitted from $KBEK_1$ and the letter L_1 from $LCE'D'L_1$. The two letters should be directly under H_1.

pressure of A with the temperature is given by the curve AD; while the corresponding partial pressure curve for the compound is given by A′D′, the temperature of the point A′ being the same as that of the point A. As the system passes along the freezing-point curve from the eutectic point with A and C as solid phases to the melting-point of pure C the partial pressure curve for the compound C is represented by the line D′E′C, while the partial pressures of A are given by the curve DC′, the temperature of the point C′ being the same as that of the point C. Starting at C and following down to the eutectic point with B and C as solid phases, the partial pressure curve for C is CE′ while the partial pressure of B which is zero at C′ increases to E at the eutectic point. Along the remaining freezing-point curve the variation in the partial pressure of B is given by EB and of C by E′B′, the temperature of the point B′ being the same as that of the point B. Along the sublimation curve with A and C as solid phases the partial pressures are given by DH_1 for the component A and $D'L_1$ for the compound C. Along the sublimation curve with C and B as solid phases the partial pressures are represented by $E'D'L_1$ for the compound and EK_1 for the component B. It will be noticed that this diagram is merely the two diagrams for A and C and for C and B. In itself it is of no importance except as a stepping stone to the next case in which the compound is partially dissociated in the solution and in the vapor.

In Fig. 4 we have the diagram for this case, partial pressure curves alone being given and the curves for univariant systems with no vapor phase being omitted as before. The curves H_1DAH, K_1EBK, $L_1D'E'CL$, B′D′ and B′E′ have the same significance as in Fig. 3. Since the compound is dissociated to a certain extent, by definition, it will no longer melt at the temperature of the point C but at the lower temperature of the points C_1, C_2 and C_3. The lowering of the partial pressure of the compound due to the dissociation at the melting-point is shown by the curve $L'C_1$. At the temperature C_1, the stable melting-point of the compound, the partial pressures of the com-

ponents A and B are not zero but are represented by C_2 and C_3 respectively. The curve C_2M represents the partial pressures of the component A in the saturated vapor in equilibrium with a solution having the same composition as the compound. C_3N is the corresponding curve for the other component while C_1L', as has already been said, gives the partial pressures of the compound under the same conditions. For the univariant system, solid A, solution and vapor, the partial pressures are represented by AD, $A'D_1$ and $A'D'$, for the component A, the component B and the compound C respectively. For the univariant system, solid compound, solution and vapor, the partial pressures are

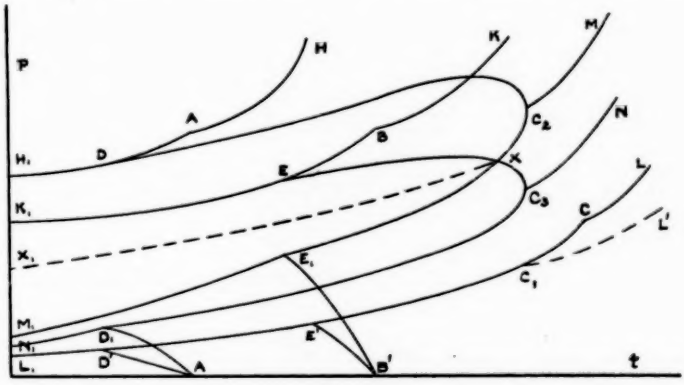


Fig. 4

represented by DC_2E_1, D_1C_3E and $D'C_1E'$, the parts DC_2, D_1C_3 and $D'C_1$ of the three curves referring to the systems in which there is not an excess of the component B in the solutions, and the parts C_2E_1, C_3E and C_1E' referring to the systems in which there is not an excess of the component A in the solutions. The curves DC_2E_2 and D_1C_3E have a true rounded maximum[1] at C_2 and C_3. Though not so drawn it is probable that the pressures of C_2 and C_3 are usually higher than those of D and E respectively. For the univariant systems, solid B, solution and

[1] Cf. van der Waals. Kon. Akad. Wetensch. Verslag, Amsterdam, 1897, 385.

vapor, the partial pressures are given by E_1B', EB and E'B', as before, the first referring to A, the second to B and the third to B. For the univariant system, solid A, solid C and vapor, the partial pressures are given by DH_1, D_1N_1 and $D'L_1$ while the partial pressures for the univariant system, solid C, solid B and vapor, the partial pressure curve for the component A is E_1M_1; for the component B it is EK_1 and for the compound C it is $E'L_1$.

If we are dealing with a compound which dissociates into two volatile components and start with the pure compound, the vapor must contain the two components in equivalent quantities. On the other hand, it is probably never the case that at the melting-point of the compound the two components are present in the vapor in exactly equivalent quantities. Such an occurrence would be tantamount to proof that there was no dissociation. There must therefore be some point at which the ratio of the components in the vapor ceases to be the same as in the compound. The diagram, Fig. 4, is so drawn as to bring out this fact clearly. At the point X the partial pressures of the two components are equal in the vapor in equilibrium with the compound. At higher temperatures this is no longer the case. If therefore we start with the pure compound at a temperature below that of the point X and allow it to vaporize to a certain extent, the partial pressure of each of the components will be represented by some point on the line X_1X. On raising the temperature the partial pressures will be represented by points on X_1X lying nearer and nearer X. When the temperature reaches that of the point X the compound will begin to liquefy and with further rise of temperature, more liquefaction will take place, the partial pressure of the component A being represented by the curve XC_2 and of the component B by the curve XC_3. The solid phase will disappear at some temperature between that of the point X and that of the points C_1, C_2 and C_3 depending on the relative masses of the solid and the vapor phase. This point X has been called by van der Waals[1] the "maximum temperature of sublimation" because it is the highest temperature at

[1] Arch. néerl. (2) 1, 78 (1897).

which the solids can be sublimed without change. Van der Waals deduced the existence of such a temperature from a consideration of his Ψ-surface; but the deduction, as given here, is much more elementary.

If the pressure of the point X lies midway between the pressures of the points C_2 and C_3, the total pressure of the system at the maximum sublimation point will be equal to the total pressure of the system at the melting-point. If the point X lies nearer C_2 than C_3, the pressure at the maximum sublimation point will be a maximum. In either of these cases the curve for the supercooled liquid will lie below the curve for the solid. This has actually been observed by Ramsay and Young with chloral ethyl alcoholate and chloral methyl alcoholate.[1] Speaking of the methyl compound they say: "It will be noticed that the liquid has apparently a lower vapour-pressure than the solid. At 35° the vapour-pressure of the solid is 17 millims, and of the liquid only 10.3 millims". With the ethyl compound the vapor-pressure of the supercooled liquid was found to be 9.8 mm at 35°, while the vapor-pressure of the solid was 24.3 mm. On the other hand, with chloral hydrate the curve for solid and vapor is so nearly a continuation of the curve for liquid and vapor that it is impossible, from the data, to tell where the freezing-point comes.

If we consider the element of time, we can draw other more interesting conclusions. Referring back to Fig. 4 we see that the equilibrium pressure for pure compound and vapor at any temperature below that of the point X will be twice the pressure P_1 of the point on XX_1 for that temperature plus the pressure P_2 represented by the point on $C_1E'D'L_1$ for that temperature. The total vapor-pressure of the system for the temperature T is therefore $P = 2P_1 + P_2$. Suppose however that the dissociation takes place slowly so that equilibrium is reached slowly and that the vapor is removed at a fairly rapid rate. In that case we can have at any moment pressures varying between P_2 and P depending on the rate of dissociation and the rate of removal of

[1] Phil. Trans. **177, I,** 82 (1886).

the vapor. The easiest way of removing the vapor is by sublimation or volatilization[1] under diminished pressure and we should therefore expect to find that in systems coming under this head the volatilization pressures would be lower than the equilibrium pressures as determined by the barometric method. We should also expect to find in some cases that no definite sublimation pressures would be obtained because the rates of formation and removal of the vapor would vary from experiment to experiment with the shape of the apparatus, the mass and surface of the solid taken, the temperature of the condenser and the rate at which heat was supplied from outside. Since slight variations in any of these factors would produce relatively large pressure changes, it would not be surprising if these disturbing influences were not recognized by investigators having no theory to guide them.

Ramsay and Young[2] found that the equilibrium pressures of aldehyde ammonia at 29°, 40°, 50° and 60° were about 13.6, 40.2, 83.6 and 307 mm respectively, while the corresponding values for the volatilization pressures were about 3.2, 7.0, 17.5 and 53 mm. Here we have a case where definite volatilization values are easily reached and, according to the theory, we should expect to find that the rate of dissociation was low. As a matter of fact it was found necessary to wait an hour or more before constant readings were obtained by the barometric method. On the other hand, with chloral hydrate the equilibrium pressure at 50° is just under 70 mm, while the sublimation pressure at this temperature was found once to be 7.4 mm and another time to be 42.0 mm. Similar results were obtained with chloral methyl alcoholate, with chloral ethyl alcoholate and with ammonium carbamate. In three of these cases equilibrium was reached in the barometric tube in times varying from two to thirty minutes, while the equilibrium pressures of ammonium carbamate were

[1] Since sublimation curve is already in use to denote a particular boundary curve I shall use volatilization-pressure to denote the pressure at which the substance volatilizes out of the distilling flask.

[2] Phil. Trans. **177**, I, 105 (1886).

not determined by Ramsay and Young. The results are thus all in harmony with the theory. The conclusion drawn by Ramsay and Young was that, in these cases, no relation between temperature and pressure was observable. This conclusion was probably the only one that could have been drawn at the time of the experiments; but it is nevertheless erroneous. In ammonium chlorid Ramsay and Young found a compound that dissociates and yet gives identical volatilization and equilibrium pressures. In this one paper of Ramsay and Young we have good instances of three of the types of dissociating compounds, in one type the volatilization curves being identical with the equilibrium curves, in another the volatilization curves being easily determined but lying below the equilibrium curves, in the third there being apparently no realizable volatilization curve.

If we can volatilize the compound at low temperatures more rapidly than it dissociates, so that we realize the curve $L_1D'E'C_1$, it is clear that on raising the temperature the compound will not start to melt at the temperature of the point X nor at the temperature of the point C_1, but will begin to melt at some temperature between that of C_1 and that of C, the latter temperature being a limiting one only to be reached in case the vapor is removed before any dissociation takes place. With a system of this sort we should expect that diminishing the pressure under which the compound volatilizes would raise the apparent melting-point. This has actually been observed by Ramsay and Young in the paper already referred to. According to the books chloral hydrate melts at 57°, this determination being due apparently to Victor Meyer.[1] On the other hand Personne[2] gives 50° as the melting-point, while Ramsay and Young[3] find the practically identical value of 50.8°, though they express it in a somewhat ambiguous form saying that "the chloral hydrate began to melt[4] and partly liquefied at 50.8". For our purposes it

[1] Meyer and Dulk. Liebig's Annalen, **175**, 75 (1874).

[2] Comptes rendus, **169**, 1363 (1869).

[3] Phil. Trans. **177**, I, 77 (1886).

[4] From the next paragraph it would appear as though 50.8° were a misprint for 50.6°.

is immaterial whether the melting-point be 51° or 57°; the important point is that no one claims a higher melting-point than 57° under atmospheric pressure. The following results were obtained by Ramsay and Young in their experiments on the temperatures of volatilization of chloral hydrate. "The bulb of a thermometer was covered by dipping it repeatedly in melted chloral hydrate, and allowing it to solidify until it had acquired a sufficiently thick deposit. A bath of sulfuric acid was used to heat the tube. The temperature rose gradually; the pressure remaining nearly constant. At 51.8° the substance was still perfectly solid, although above its ordinary melting-point, 50.6°, the pressure registered 11.4 millims. The temperature then rose to 57° while the pressure rose to 12.3 millims; after this the pressure rose only 0.1 millim, while the temperature rose to 64°. Even at 64° no sign of melting was to be noticed. The experiment was then discontinued and the melting-point of the sublimed chloral hydrate compared with that of the portion left on the thermometer. It was 50.6° for both. The substances had therefore undergone no change on heating. It is right to observe, however, that a specimen of chloral hydrate, which had been repeatedly melted, and which was examined after two years, left on treatment with water an insoluble residue, the melting-point of which was above 130°. The melting-point of the residue on the thermometer-bulb, however, showed that it did not consist of this substance, which is possibly a polymeride."

One possible explanation of this phenomenon of the chloral hydrate remaining solid at 64° is to attribute it to experimental error on the ground that the thermometer was heated by conduction and did not register the temperature of the solid. In view of Carnelley's experience with ice and with mercuric chlorid,[1] the possibility of such an error cannot be denied. On the other hand it must be remembered that Ramsay and Young have had much experience in determining volatilization pressures and temperatures and it would therefore be a most extra-

[1] Proc. Roy. Soc. **31**, 284 (1881); Chem. News, **42**, 130, 313 (1880); **45**, 39 (1882); Nature, **23**, 341 (1881); Jour. Chem. Soc. **41**, 317 (1882).

ordinary coincidence if they should make a serious error in the one case in which Duhem's theory accounts satisfactorily for the observed facts. In another experiment in which the temperature was raised only to 55° Ramsay and Young say: "After this experiment, the chloral hydrate adhering to the bulb of the thermometer was carefully examined, and it was found that the bulb was completely coated, and that the substance was in perfect contact with it. The minimum thickness was 0.8 millim, and the hydrate extended 12 millims below the bulb and about 30 millims above it. The hydrate was therefore undoubtedly heated above its usual melting-point without melting."

It is unfortunate that in this particular experiment the temperature was not carried above 57° and also that reference is nowhere made in the article to the possibility of 57° being the temperature at which chloral hydrate melts.[1] For all that, it appears reasonably certain that the heating of solid chloral hydrate to 64° was an actual fact and that we have here an actual case of the kind required by the theory in which the melting-point of a compound can be raised by volatilizing under diminished pressure.[2]

The pressure-temperature diagram for a system in which there is complete dissociation in the vapor phase differs from Fig. 4, provided there is a maximum sublimation temperature, only by not having the curves $L_1D'E'C_1CL$, C_1L', $A'D'$ and $B'E'$, the curves showing the partial pressures of the compound. For this reason it is not worth while to reproduce it here. We may however get a clearer idea of the relation between the maximum sublimation temperature and the concentration in the solution phase if we consider the concentration-temperature diagram for liquid and vapor phases. This is given in Fig. 5, the assumption being made that the compound melts at a lower tempera-

[1] Experiments on the melting-point of this substance are now being carried on in my laboratory.

[2] There is no reason for assuming the formation of the so-called isomeric chloral hydrate melting at 80°, obtained by Meyer and Dulk. Liebig's Annalen, 175, 5 (1874).

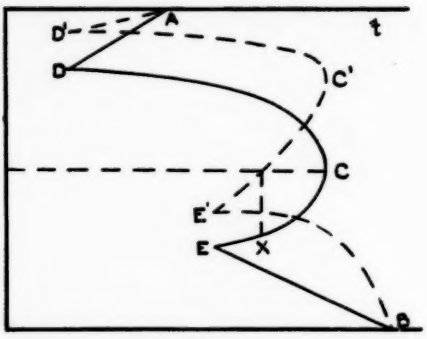


Fig. 5

ture than the component B. This diagram also expresses the facts for the case in which there is not complete dissociation in the vapor phase provided we consider equilibrium phenomena only. The curves AD, DCE and EB give the concentrations in the liquid phase, while the dotted curves AD′, D′C′E′ and E′B give the simultaneous concentrations in the vapor phase. At the temperature of the point X the ratio of the components in the vapor is the same as in the compound. At all temperatures not exceeding this, the compound will sublime unchanged. If the temperature is raised above that of the point X, the solid will begin to melt forming at first the solution denoted by the point X. As the distillation goes on the system will pass along the curve XC in the direction of C, the distillate containing relatively more of the component A than the compound. We have sufficient data to determine approximately the maximum sublimation temperature for iodin monochlorid.[1] The stable form of this compound melts at 27.2°. At this temperature the ratio of chlorin to iodin in the vapor is 1.04, while at 15° the ratio is only 0.93. By interpolation we find that the ratio is unity at 24° ± 1°. At temperatures below 24° iodin monochlorid will sublime without change. Between 24° and 27.2° the compound will liquefy and the distillate will contain relatively more chlorin than the compound.

[1] Stortenbeker. Zeit. phys. Chem. **3**, 11 (1889).

The pressure-temperature diagram for a compound, stable at its melting-point, completely dissociated in the vapor and having no maximum sublimation temperature is given in Fig. 6.

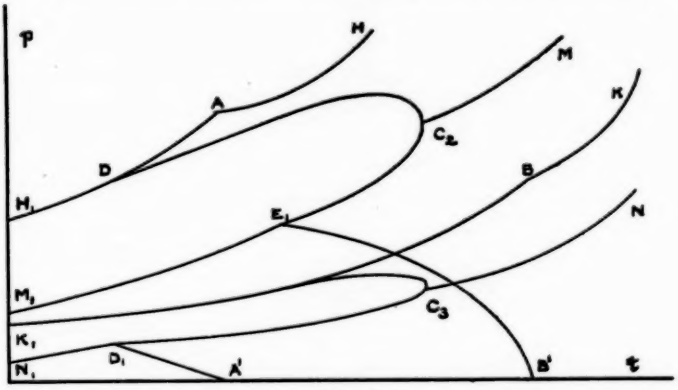


Fig. 6

The letters have the same significance as in Fig. 4.[1] The distinction between this case and the preceding one is that here the curves C_2E_1 and C_3E do not intersect, and there is therefore no temperature at which the component will sublime without change. This system could be realized with a hydrated salt stable at its melting-point. None of the hydrates of ferric chlorid will sublime unchanged at any temperature. Whether they effloresce or deliquesce depends on the temperature of the experiment; but in either case they lose water. From the diagram we see that if the temperature is below that of the points E and E_1 a second solid phase will appear. If the temperature is between that of the point E and that of the point C_3 the compound will liquefy. A maximum sublimation temperature of a new type would be possible in case E_1M_1 were to cut EK_1. At temperatures below that of the intersection, the solid would sublime without change. Above the maximum sublimation temperature a second solid phase would appear. This new

[1] The letter E_1 is missing from the curve BE_1K_1.

type of maximum sublimation temperature might also be realized with compounds like $HgI_2 2AgI$, which cannot exist in equilibrium with any mixture of the fused components.

The concentration-temperature diagram corresponding to the pressure-temperature diagram in Fig. 6 is given in Fig. 7.

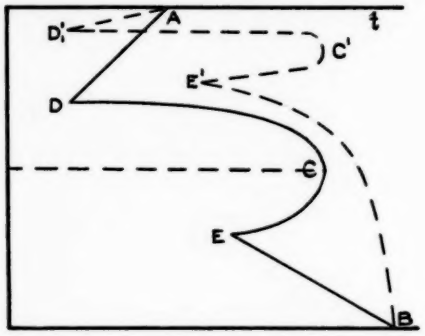


Fig. 7

The letters have the same significance as in Fig. 5. From this diagram it will be seen that the ratio of the components in the vapor is the same as the ratio in the compound only when the component B is present as solid phase. There is therefore no maximum sublimation temperature. If we wished to indicate the existence or non-existence of a maximum sublimation temperature of the second type, we could do so by drawing lines from D′ and E′ showing the percentage compositions of the vapors in equilibrium with A and C as solid phases and B and C as solid phases respectively. If either of these curves cut the dotted line through C, there would be a maximum sublimation temperature, otherwise not.

Another pressure-temperature diagram that we have to consider is the one for a system in which there is complete dissociation in the vapor and the compound is not stable at its melting-point. The diagram is given in Fig. 8.[1] As usual the boundary curves for pure A are represented by H_1DAH and for

[1] The upper E should be E_1 and the lower B B′.

pure B by K_1EBK. When the phases are solid A, solution and vapor the partial pressures are given by AD and $A'D_1$; when the phases are solid compound, solution and vapor, the partial pressures are given by DE_1 and D_1E; when the phases are solid B, solution and vapor, the partial pressures are given by E_1B' and EB while DH_1 and D_1N_1, E_1M_1 and EK_1 are the pairs of curves for the system solid A, solid compound and vapor, and for the system, solid B, solid compound and vapor respectively, the first-mentioned curve giving throughout the partial pressures of A and the second the partial pressures of B. This diagram could be realized with sodium sulfate and water. It is to be noticed that the curves DE_1 and M_1E_1 meet at an angle because

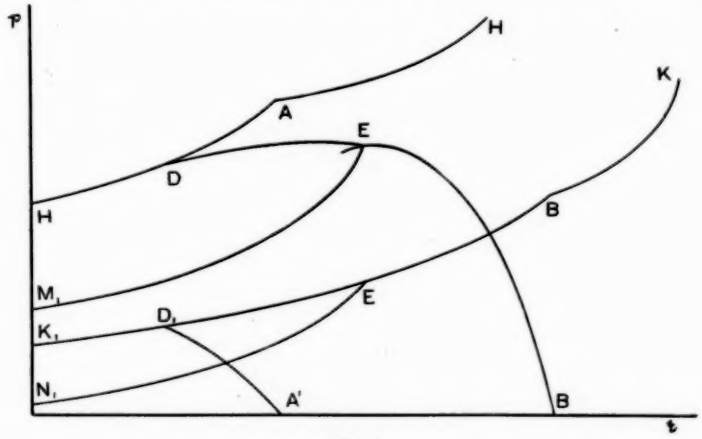


Fig. 8

they refer to different univariant systems. In the case of a salt and water the curve $B'E_1$ will have a distinct pressure maximum; but that is not necessarily the case for all systems of this class. In all cases the metastable prolongation of $B'E_1$ will lie below DE_1. This point has already been discussed in a preceding paper[1] so that a reference here will suffice. It is to be noticed that a compound instable at its melting-point cannot have a

[1] Jour. Phys. Chem. 3, 1 (1899).

maximum sublimation temperature of the first type, though it may have one of the second.

Before closing this rather long paper it will be necessary to consider a curious phenomenon discovered by Ramsay and Young. The equilibrium pressures of phthalic acid and still more of succinic acid, as determined by the barometric method, vary with the amount of acid taken. I quote what Ramsay and Young say about the pressures of dissociation of succinic acid in a barometric tube.[1] "A very large number of experiments were made with this substance. In the first three series the numbers obtained gave, when graphically represented, curves with double flexure; and so long as the same amount of substance was employed recombination at any given temperature reached the same point as regards pressure as did decomposition. The curves obtained from these series were fairly concordant. But, on increasing the amount of substance, the pressures for given temperatures were much higher, and the double flexure tended to disappear. With phthalic acid it is possible that the vertical[2] trend of the curve might have been due to an insufficient amount of substance; but this cannot have been the case with succinic acid. As the pressure of dissociation of succinic acid appears to depend on the amount of substance present, and is capable of being altered at will, and as the number of experiments made on this subject comprise several thousand readings, and lasted over six weeks, we content ourselves with reproducing the results in the form of curves. It may be generally stated that the larger the amount of substance the higher the pressure at which the double flexure appears. It may possibly be that succinic acid has the power of forming intermediate anhydrides of some such type as $COOH.C_2H_4.CO.O.CO.C_2H_4.COOH$, and that its abnormal behavior is to be accounted for on the supposition of their existence, but this is merely a conjecture."

From the plotted curves it appears that for a given temperature, differences in pressure of as much as 100 mm are to

[1] Phil. Trans. **177**, I, 103 (1886).

[2] Ramsay and Young measure pressures along the abscissas instead of along the ordinates as is usually done.

be observed, the higher pressures corresponding to the larger amounts of succinic acid. These results are so very surprising that they must be explained. We may reject the hypothesis of an intermediate anhydrid at once. While we cannot prove that such a compound is not formed, the assumption does not help us in any way and may therefore be discarded as superfluous so far as the facts before us are concerned. The facts to be explained are that at the same temperature different pressures are obtained by varying the amount of substance taken. Since we are dealing with a two-component system there can only be two phases because such a phenomenon is impossible with three phases. The vapor phase is certainly one of the two, and as the discrepancies are noticed at temperatures as low as 80°, the other phase cannot be a liquid phase. The conclusion is therefore forced upon us that there is only one solid phase. Since the solid mass contains both succinic acid and succinic anhydrid, these two substances must form solid solutions. It has already been pointed out that Mr. Brown's data for the freezing-points of phthalic anhydrid and phthalic acid point to the formation of a series of solid solutions. Since Ramsay and Young find the same phenomena with phthalic acid as with succinic acid, there seems no reason to doubt that succinic acid and succinic anhydrid do crystallize together,[1] especially as no other hypothesis is possible. Assuming the formation of solid solutions, it becomes a simple matter to explain the phenomena. The vapor given off by succinic acid in the barometer tube consists chiefly of water. If we have a vapor phase of constant volume a certain amount of succinic acid will be dissociated. The residual amount of anhydrid will be a smaller percentage of the total solid, the more succinic acid is taken. With large amounts of succinic acid we should therefore get dilute solutions of anhydrid in the acid and therefore a higher vapor-pressure. This is exactly what was found by Ramsay and Young. Of course, if the vapor phase is not kept constant in amount, there will be minor fluctuations due to this. The smaller the vapor phase,

[1] There is nothing in the crystalline forms of succinic acid and succinic anhydrid to make this hypothesis improbable.

the less water will evaporate from the solid mass and the more dilute will be the solid solution formed. As Ramsay and Young give no numerical data, it is impossible to tell whether this variation was an important factor in their experiments or whether the discrepant results are to be referred solely to the variation in the mass of the solid phase. That, however, is a question of no real importance. The double flexure in the curves undoubtedly begins at the temperature at which the solid solution is entirely melted. One curious feature about the curves is that the double flexures occur between the temperatures of 180° and 184° while succinic acid melts, according to Ramsay and Young, at 181°. At first sight this seems to negative the explanation of the double flexures just offered; but this difficulty is not serious. The melting-point of 181° is undoubtedly, though not so stated, the stable melting-point of succinic acid with no vapor phase or a relatively small one. Under these circumstances, the dissociation products are present in the melt in equivalent quantities. If we increase the vapor phase, water vaporizes and if there were no further dissociation in the solution it would become more dilute and the freezing-point would rise. Of course, as the water vaporizes more acid will dissociate; but it is quite conceivable that at first the diluting due to the vaporization might more than counterbalance the concentrating of the solution due to the further dissociation of the acid. If the measurements of Ramsay and Young are to be taken as accurate, this must be the case.

The main features of this paper may be re-stated as follows:

1. There has been a general discussion of pressure-temperature diagrams for two-component systems in which a compound is formed.

2. Duhem's theory of 'permanent changes' has been shown to be of great value in studying these systems.

3. Explanations have been found for the interesting phenomena recorded by Ramsay and Young in a paper entitled On Evaporation and Dissociation, Part I.

Cornell University, December, 1898

THE ELECTROMOTIVE FORCES OF CONCENTRATION CELLS

BY J. E. TREVOR

The electromotive force of a concentration cell without diffusion is proportional to the thermodynamic temperature, only when the heat of dilution of its solutions, from the one concentration to the other, is negligibly small. In general, however, this heat of dilution is not negligible; and it may be shown that the consequent departure from proportionality between electromotive force and temperature is determined wholly by the form of the heat of dilution, regarded as a function of the temperature and the concentrations of the two solutions of the cell.

When the quantity of electricity ϵ is passed through one of the elements of the cell, under an applied electromotive force π infinitesimally greater than that developable by the element, the energy $\mathbf{E}$ of the solution in the cell is changed reversibly by the amount of the electric work-equivalents $\pi d\epsilon$, and the thermal work-equivalents $\theta d\eta$, that are added:

$$d\mathbf{E} = \pi d\epsilon + \theta d\eta.$$

Here η represents the entropy of the solution, and θ its thermal potential (thermodynamic temperature). If the mass m_1 of the water in the element is varied also, the chemical work-equivalents $\mu_1 dm_1$ will be added to the change of the energy; which latter will therefore be, in general,

$$d\mathbf{E} = \pi d\epsilon + \theta d\eta + \mu_1 dm_1. \qquad (1)$$

It is hereby supposed that the mass m_2 of the dissolved electrolyte is not varied independently. Its change is understood to be completely determined by the quantity of electricity passing: thus we have

$$d\epsilon = dm_2/a, \qquad (1a)$$

where α is the quantity of electricity associated with the dissolving of unit m_2. Eliminating $d\epsilon$ between (1) and (1*a*), we get

$$d\mathbf{E} = \theta d\eta + \mu_1 dm_1 + \frac{\pi}{\alpha} dm_2. \tag{2}$$

Here the entropy and the masses appear as our independent variables. But it is desirable to have the temperature and masses independent; and this we obtain by subtracting $\eta d\theta$ from both sides of (2), finding

$$d(\mathbf{E} - \theta\eta) = -\eta d\theta + \mu_1 dm_1 + \frac{\pi}{\alpha} dm_2. \tag{3}$$

The quantity

$$\mathbf{F} = \mathbf{E} - \theta\eta \tag{3a}$$

is Helmholtz's 'free energy'. It appears here, because of (3), as a function

$$\mathbf{F}(\theta, m_1, m_2) \tag{4}$$

of the temperature and the masses of the two independently variable components of the solution in the cell.

The quantity $\mathbf{E}$, in (3*a*), is also a function of these same variables. For we have

$$\mathbf{E} = \mathbf{F} + \theta\eta,$$

or, expressing η as a derivative of $\mathbf{F}$, from (3),

$$\begin{aligned} \mathbf{E} &= \mathbf{F} - \theta \frac{\partial \mathbf{F}}{\partial \theta} \\ &\equiv \mathbf{E}(\theta, m_1, m_2). \end{aligned} \tag{5}$$

Eliminating the entropy η between the foregoing equations

$$\left.\begin{aligned} \mathbf{F} &= \mathbf{E} - \theta\eta \\ \frac{\partial \mathbf{F}}{\partial \theta} &= -\eta, \end{aligned}\right\}$$

and noting the results expressed in (4) and (5), we find

$$\mathbf{F}(\theta, m_1, m_2) = \mathbf{E}(\theta, m_1, m_2) + \theta \frac{\partial}{\partial \theta} \mathbf{F}(\theta, m_1, m_2);$$

or, more simply,

$$\frac{\partial \mathbf{F}}{\partial \theta} - \frac{\mathbf{F}}{\theta} = -\frac{\mathbf{E}}{\theta}.$$

Here, very fortunately, the two terms of the first member can be united into a single expression, by taking advantage of the fact that, identically,

$$\frac{\partial \mathbf{F}}{\partial \theta} - \frac{\mathbf{F}}{\theta} = \theta \frac{\partial}{\partial \theta} \cdot \frac{\mathbf{F}}{\theta}.$$

For, eliminating the first members between these two equations, we obtain

$$\frac{\partial}{\partial \theta} \cdot \frac{\mathbf{F}(\theta, m_1, m_2)}{\theta} = -\frac{\mathbf{E}(\theta, m_1, m_2)}{\theta^2}. \tag{6}$$

Now, the electromotive force π of our single element is proportional to the m_2-derivative of the function $\mathbf{F}$. For, from (3) we have

$$\frac{\pi}{a} = \frac{\partial \mathbf{F}}{\partial m_2}. \tag{7}$$

Differentiating (6) with respect to m_2, for the purpose of getting π into the relation (6), we find

$$\frac{\partial}{\partial \theta}\left(\frac{1}{\theta}\frac{\partial \mathbf{F}}{\partial m_2}\right) = -\frac{1}{\theta^2}\frac{\partial \mathbf{E}}{\partial m_2}. \tag{8}$$

Before applying this equation (8), between

$$\frac{\partial \mathbf{F}}{\partial m_2} \quad \text{and} \quad \frac{\partial \mathbf{E}}{\partial m_2},$$

to the two elements of a concentration cell, we may note with advantage that these two derivatives are functions of the temperature θ and the relative mass $m_1/m_2 = h$ of the water. This appears as follows. Denoting by $\mathbf{e}$ and $\mathbf{f}$ the energy and free energy of unit mass of the solution, we have, for this mass,

$$\left.\begin{aligned} \mathbf{f} &= \mathbf{F}(\theta, m_1, m_2) \\ m_1 + m_2 &= 1 \\ m_1/m_2 &= h; \end{aligned}\right\} \qquad \left.\begin{aligned} \mathbf{e} &= \mathbf{E}(\theta, m_1, m_2) \\ m_1 + m_2 &= 1 \\ m_1/m_2 &= h; \end{aligned}\right\}$$

from which, eliminating m_1 and m_2 between the equations of each set, we find

$$\mathbf{f} \equiv \mathbf{f}(\theta, h). \qquad \mathbf{e} \equiv \mathbf{e}(\theta, h).$$

Now, since

$$\left.\begin{aligned}\mathbf{F}(\theta, m_1, m_2) &= (m_1 + m_2)\cdot\mathbf{f}(\theta, h),\\ \mathbf{E}(\theta, m_1, m_2) &= (m_1 + m_2)\cdot\mathbf{e}(\theta, h),\end{aligned}\right\}$$

we find, for our mass-derivatives,

$$\left.\begin{aligned}\frac{\partial \mathbf{F}}{\partial m_2} &= \mathbf{f}(\theta, h) + (m_1 + m_2)\frac{\partial \mathbf{f}}{\partial h}\frac{\partial h}{\partial m_2},\\ \frac{\partial \mathbf{E}}{\partial m_2} &= \mathbf{e}(\theta, h) + (m_1 + m_2)\frac{\partial \mathbf{e}}{\partial h}\frac{\partial h}{\partial m_2},\end{aligned}\right\}$$

or, since $h = m_1/m_2$, and therefore $\partial h/\partial m_2 = -m_1/m_2^2$, we have, identically,

$$\frac{\partial \mathbf{F}}{\partial m_2} \equiv \frac{\partial \mathbf{F}}{\partial m_2}(\theta, h), \tag{9a}$$

$$\frac{\partial \mathbf{E}}{\partial m_2} \equiv \frac{\partial \mathbf{E}}{\partial m_2}(\theta, h), \tag{9b}$$

as stated. In equation (7), accordingly, we have

$$\frac{\partial \mathbf{F}}{\partial m_2} = \frac{\pi(\theta, h)}{a}; \tag{10}$$

and (8) becomes, through elimination of $\partial \mathbf{F}/\partial m_2$ between (8) and (10),

$$\frac{\partial}{\partial \theta}\cdot\frac{\pi(\theta, h)}{\theta} = -\frac{a}{\theta^2}\cdot\frac{\partial \mathbf{E}}{\partial m_2}(\theta, h). \tag{11}$$

Integrating (11), between any fixed temperature of reference θ_0 and the general value θ of the temperature, gives

$$\frac{\pi(\theta, h)}{\theta} - \phi(\theta, h) = \frac{\pi(\theta_0, h)}{\theta_0} - \phi(\theta_0, h), \tag{12}$$

where

$$\frac{\partial \phi}{\partial \theta} = -\frac{a}{\theta^2}\cdot\frac{\partial \mathbf{E}}{\partial m_2}(\theta, h);$$

whence it appears that the first member of (12) is independent of θ, and we have

$$\frac{\pi}{\theta} - \phi(\theta, h) = k(h),$$

or

$$\pi = \theta\cdot k(h) + \theta\cdot\phi(\theta, h). \tag{13}$$

According to this equation, the electromotive force is proportional to the thermodynamic temperature when the heat of dilution $\partial \mathbf{E}/\partial m_2$ becomes negligibly small. For then the quantity ϕ becomes a function of h alone, and, therefore,

$$\pi = \theta[k(h) + \phi(h)].$$

Otherwise, the relation of the electromotive force to the temperature is the more complicated one indicated by the general equation (13). So, the departure of the electromotive force from proportionality with the temperature is determined wholly by the form of the heat of dilution, as a function of the temperature and the concentration of the solution.

A similar conclusion can be reached in regard to the electromotive force

$$\pi(\theta, h_2) - \pi(\theta, h_1) = \Pi(\theta, h_1, h_2)$$

of a concentration cell, without diffusion, made up of two elements having different values h_1 and h_2 of the concentration h. We assume

$$h_2 > h_1.$$

For such a cell the fundamental equation (11) above becomes

$$\frac{\partial}{\partial \theta} \cdot \frac{\Pi(\theta, h_1, h_2)}{\theta} = -a \frac{\dfrac{\partial \mathbf{E}}{\partial m_2}(\theta, h_2) - \dfrac{\partial \mathbf{E}}{\partial m_2}(\theta, h_1)}{\theta^2} = \frac{-\Delta(\theta, h_1, h_2)}{\theta^2}, \tag{14}$$

when, for brevity, we denote by Δ the heat of dilution

$$a \int_{h_1}^{h_2} \frac{\partial}{\partial h} \left(\frac{\partial \mathbf{E}}{\partial m_2} \right) dh.$$

Integrating (14) from θ_0 to θ, we find

$$\frac{\Pi(\theta, h_1, h_2)}{\theta} - \mathrm{F}(\theta, h_1, h_2) = \frac{\Pi(\theta_0, h_1, h_2)}{\theta_0} - \mathrm{F}(\theta_0, h_1, h_2), \tag{15}$$

in which the function F satisfies the relation

$$\frac{\partial \mathrm{F}}{\partial \theta} = -\frac{\Delta}{\theta^2}. \tag{15a}$$

The value of the first member of (15) being independent of the temperature, we may write the equation in the form

$$\frac{\Pi}{\theta} - F(\theta, h_1, h_2) = K(h_1, h_2); \qquad (16)$$

or, for the general value of the electromotive force,

$$\Pi = \theta \cdot K(h_1, h_2) + \theta \cdot F(\theta, h_1, h_2). \qquad (17)$$

It appears from this equation (17), as from equation (13) above, that the electromotive force is directly proportional to the thermodynamic temperature, only when the heat of dilution Δ is negligibly small. For, then, F becomes a function of the h's alone, which converts the equation into

$$\Pi = \theta[K(h_1, h_2) + F(h_1, h_2)].$$

When Δ is not negligible, the relation between the electromotive force and the temperature is given by the more complicated equation (17). So, it is seen that the departure of the electromotive force from proportionality with the temperature depends wholly upon the form of the function

$$\Delta(\theta, h_1, h_2).$$

In order to utilize the above equation (17) for the calculation of the electromotive forces of our concentration cells, it is necessary to determine, presumably from direct experiment, the form of the heat of dilution of the solutions of the electrolyte employed—the function $\Delta(\theta, h_1, h_2)$. For a given h_1 and h_2, for example, the observed values of Δ at a series of temperatures can be expressed as a function $\Delta(\theta)$; wherefrom, by integration, the corresponding value of the function $F(\theta)$ is found. The next step will be to determine, by direct measurement, the value Π_1 of Π for the given h_1 and h_2 at any fixed temperature θ_1 in the series through which the function $\Delta(\theta)$ holds good; whereby the data are given for determining the numerical value of K by means of the relation (16),

$$K = \Pi_1/\theta_1 - F(\theta_1).$$

Having this value of K, the value of the electromotive force Π

at any temperature in the series can be calculated at once from the general equation (17)

$$\Pi = \theta \cdot \mathrm{K} + \theta \cdot \mathrm{F}(\theta).$$

The process may then be repeated for any other pair of values of h; and for any other electrolyte.

More generally, if an empirical formula is determined for the heat of dilution

$$\Delta(\theta, h_1, h_2),$$

for a series of values of the h's as well as a series of the temperatures, the corresponding form of the function

$$\mathrm{F}(\theta, h_1, h_2)$$

can be found by integration; whereupon there will remain merely to make some one measurement of Π in order to find, by the relation (16), the corresponding form of the function $\mathrm{K}(h_1, h_2)$,

$$\mathrm{K}(h_1, h_2) = \Pi_1/\theta_1 - \mathrm{F}(\theta_1, h_1, h_2).$$

Having, thus, formulas for F and K, the value of Π can be calculated, for any of the temperatures and pairs of values h_1, h_2 for which the originally determined form of $\Delta(\theta, h_1, h_2)$ holds, from the general equation (17),

$$\Pi = \theta \cdot \mathrm{K}(h_1, h_2) + \theta \cdot \mathrm{F}(\theta, h_1, h_2).$$

The heat of dilution

$$\Delta = a \int_{h_1}^{h_2} \frac{\partial}{\partial h}\left(\frac{\partial \mathrm{E}}{\partial m_2}\right) dh$$

$$= \frac{\partial \mathrm{E}}{\partial m_2/a}(\theta, h_2) - \frac{\partial \mathrm{E}}{\partial m_2/a}(\theta, h_1)$$

of our concentration cell will be zero if the heat of dilution be zero in each element:

$$\frac{\partial \mathrm{E}}{\partial m_2}(\theta, h_2) = \frac{\partial \mathrm{E}}{\partial m_2}(\theta, h_1) = 0;$$

or if it have the same value in both elements:

$$\frac{\partial \mathrm{E}}{\partial m_2}(\theta, h_2) = \frac{\partial \mathrm{E}}{\partial m_2}(\theta, h_1).$$

In either case, the electromotive force of the cell is proportional to the thermodynamic temperature. This result, however, is but a particular case of the general fact that, when the energy difference of two states of a system is negligibly small, the corresponding difference of the free energy is proportional to the thermodynamic temperature. We have, namely, for the free energy of either state,

$$\mathbf{F} = \mathbf{E} + \theta \frac{\partial \mathbf{F}}{\partial \theta};$$

and for the difference of the two,

$$(\mathbf{F}_2 - \mathbf{F}_1) = (\mathbf{E}_2 - \mathbf{E}_1) + \theta \frac{\partial}{\partial \theta} (\mathbf{F}_2 - \mathbf{F}_1);$$

whence, for $\mathbf{E}_2 - \mathbf{E}_1 = 0$,

$$\mathbf{F}_2 - \mathbf{F}_1 = \text{const.} \times \theta.$$

In a recent experimental study of the electromotive forces of concentration cells without diffusion, Mr. Hamilton P. Cady has found that, in certain cases, the electromotive forces of the cells appear as the sum,

$$\Pi = \theta \cdot \mathrm{R} \log \frac{h_2}{h_1} + \Delta, \tag{18}$$

of the value

$$\theta \cdot \mathrm{R} \log \frac{h_2}{h_1},$$

assigned by the osmotic theory for the particular case of negligibly small heat of dilution Δ, and the observed heat of dilution Δ itself. We may ask how the temperature θ must enter into the function $\Delta(\theta, h_1, h_2)$ for this to be the case. Writing (18) in the form

$$\frac{\Pi}{\theta} = \mathrm{R} \log \frac{h_2}{h_1} + \frac{\Delta}{\theta}, \tag{19}$$

and eliminating Π/θ between (19) and the general equation (16),

$$\frac{\Pi}{\theta} - \mathrm{F}(\theta, h_1, h_2) = \mathrm{K}(h_1, h_2),$$

we find

$$\frac{\Delta}{\theta} = \left[\mathrm{K}(h_1, h_2) - \mathrm{R} \log \frac{h_2}{h_1}\right] + \mathrm{F}(\theta, h_1 h_2).$$

Differentiating with regard to θ, and comparing with (15*a*), gives

$$\frac{\theta \frac{\partial \Delta}{\partial \theta} - \Delta}{\theta^2} = \frac{\partial F}{\partial \theta}$$

$$= -\frac{\Delta}{\theta^2};$$

that is to say,

$$\frac{\partial \Delta}{\partial \theta} = 0,$$

or

$$\Delta = f(h_1, h_2).$$

So the necessary condition antecedent to Mr. Cady's result is that the heat of dilution Δ shall not contain the temperature.

For such cases our initial differential equation (14),

$$\frac{\partial}{\partial \theta} \cdot \frac{\Pi}{\theta} = -\frac{\Delta}{\theta^2},$$

integrates to

$$\frac{\Pi}{\theta} - \frac{f(h_1, h_2)}{\theta} = K(h_1, h_2),$$

which is a particular case of the general integral equation (16); and herefrom follows, on comparing with (19),

$$K(h_1, h_2) = R \log \frac{h_2}{h_1}.$$

For cases such as those studied by Mr. Cady, therefore, we have

$$\frac{\Pi}{\theta} - \frac{f(h_1, h_2)}{\theta} = R \log \frac{h_2}{h_1},$$

or

$$\Pi - f(h_1, h_2) = \theta \cdot R \log \frac{h_2}{h_1}.$$

That is to say, we discover how the h's enter into the *difference* of Π and Δ, but we learn nothing about the manner in which the h's enter into the heat of dilution f.

Although we know nothing concerning the form of the function

$$\Delta(\theta, h_1, h_2),$$

yet it may be not without interest to find the shape which our general equation (17)

$$\Pi = \theta \cdot \mathrm{K}(h_1, h_2) + \theta \cdot \mathrm{F}(\theta, h_1, h_2), \qquad (17)$$

assumes under simple assumptions regarding the form of Δ. Let it be recalled that the function $\mathrm{F}(\theta, h_1, h_2)$ is defined by the relation

$$-\int_{\theta_0}^{\theta} \frac{\Delta(\theta, h_1, h_2)}{\theta^2} d\theta = \mathrm{F}(\theta, h_1, h_2) - \mathrm{F}(\theta_0, h_1, h_2) + [k(h_1, h_2, c) - k(h_1, h_2, c)],$$

where c is a numerical constant and the square bracket is zero.

(*a*) *Assume* $\Delta = 0$

Under this familiar assumption, that Δ contains neither θ, h_1, h_2, nor a constant, the quantity

$$-\frac{\Delta}{\theta^2} d\theta$$

becomes $0 d\theta$; whence follows

$$\mathrm{F}(\theta, h_1, h_2) = 0,$$

and, from the above equation (17),

$$\Pi = \theta \cdot \mathrm{K}(h_1, h_2); \qquad (20)$$

in which it may be permissible to assume that $\theta \mathrm{K}$ is identically $\mathrm{R}\theta \log (h_2/h_1)$.

(*b*) *Assume* $\Delta = f(h_1, h_2)$

This case has already been considered above. Under its supposition, that Δ does not contain the temperature, we have the quantity

$$-\frac{\Delta}{\theta^2} d\theta$$

becoming

$$-\frac{f(h_1, h_2)}{\theta^2} d\theta;$$

whence

$$F(\theta, h_1, h_2) = \frac{f(h_1, h_2)}{\theta};$$

and, from (17),

$$\Pi = \theta \cdot K(h_1, h_2) + f(h_1, h_2), \tag{21}$$

as before. If we here put

$$\Delta = f = 0,$$

the equation reduces to the preceding equation (20); as it should, since the former assumption is but a special case of the latter.

(*c*) *Assume* $\Delta = f(h_1, h_2) \cdot \theta$

If Δ were directly proportional to the thermodynamic temperature, we should have

$$-\frac{\Delta}{\theta^2}\, d\theta = -\frac{f(h_1, h_2)}{\theta}\, d\theta;$$

wherefore

$$F(\theta, h_1, h_2) = -f(h_1, h_2) \cdot \log \theta;$$

and, from (17),

$$\Pi = \theta \cdot K(h_1, h_2) - \theta \log \theta \cdot f(h_1, h_2). \tag{22}$$

If Δ were inversely proportional to the temperature, we should have

$$\Delta = f(h_1, h_2)/\theta;$$

and, in consequence,

$$\Pi = \theta \cdot K(h_1, h_2) + \frac{1}{2}\frac{f(h_1, h_2)}{\theta}. \tag{23}$$

Corresponding to the case (*a*), that of zero heat of dilution, the temperature coefficient of the electromotive force is

$$\frac{\partial \Pi}{\partial \theta} = K(h_1, h_2); \tag{20'}$$

which is found by differentiating (20). The temperature coefficient in the second case, when the heat of dilution does not

contain the temperature, is identical with this. In the third and fourth cases we find

$$\frac{\partial \Pi}{\partial \theta} = [K(h_1, h_2) - f(h_1, h_2)] - \log \theta \cdot f(h_1, h_2); \qquad (22')$$

$$\frac{\partial \Pi}{\partial \theta} = K(h_1, h_2) - \frac{1}{2} \frac{f(h_1, h_2)}{\theta^2}.$$

From the way in which the temperature coefficient varies with the temperature, it may often be possible to draw some conclusion regarding the manner in which the temperature enters into the heat of dilution.

It may be pointed out, in closing, that the part played by the heat of dilution of a solution, in the relation between the vapor pressure, the concentration, and the temperature of the solution, obviously can be investigated in a way wholly analogous to that pursued above.

Cornell University

CORRECTION

BY WILDER D. BANCROFT

An unfortunate error has occurred in Mr. Cady's paper on the Electromotive Force between Amalgams.[1] It is there pointed out that the work done in carrying one reacting weight of dissolved zinc from one concentration to another is the same whether the zinc has the formula Zn_1, Zn_2 or Zn_x. While this is true, the quantity of electricity[2] necessary to transport one reacting weight of Zn_2 is double that necessary to transport one reacting weight of Zn_1. The electromotive force of the cell in the case of Zn_2 existing in the amalgam would be one-half that of a cell in which Zn_1 existed in the amalgam.[3] The electromotive force does show the degree of complexity in the amalgam provided the heat of dilution is zero. The responsibility for the mistake is mine. The error does not affect the important part of Mr. Cady's paper.

[1] Jour. Phys. Chem. **2**, 554 (1898).

[2] Cf. Le Blanc. Electrochemistry, 159.

NEW BOOKS

Die Erhaltung der Arbeit. *By Richard Heger. 16 × 24 cm; pp. vi and 305. Hannover: Helwingsche Verlagsbuchhandlung, 1896. Price: paper 8 marks.* — The author's purpose is to describe different forms of energy, their transference, and their conversion into other forms, from the point of view of the indestructibility of energy, in a way readily understood by readers little conversant with mathematics and less with any science.

The first third of the book is devoted to simple examples of mechanics, pulleys, levers, inclined planes, falling bodies, elastic vibrations, hydrostatics, water wheels, etc., such as may be found in any elementary textbook of physics. The next third treats of the gas laws, hot air engine and steam engine, and the last third consists mainly of descriptions of galvanometers and dynamos and elementary notions of electricity.

Great pains are taken to employ only common expressions and to exclude all scientific terms and 'foreign words' whenever it is possible. In principle this is praiseworthy, and it is not pleasant to find new words coined or borrowed from other languages when their equivalents already exist in one's own, but new ideas often require new words and a too determined sticking to the vocabulary of a century ago may lead to confusion rather than clearness. The use of *Raum* instead of *Volum*, of *Beständige* instead of *Konstant*, of *Fassung* instead of *Kapazität*, is perhaps excusable; the use of *Wärmedicht* (on the plan of air-tight so here 'heat-tight') for adiabatic is ingenious; but it is decidedly disturbing to find electric 'potential' classed as a strange word and for this substituting the term *Arbeitsgrad*. Not much more agreeable is it to read of a zero needle (*Nullnadel*) where an astatic needle is meant, or of Daniel beakers and Bunsen beakers, for Daniel cells and Bunsen cells. In one case at least this exaggerated determination to employ no new term has led the author into serious error. The word energy does not occur in the book. *Arbeit*, that is, work, is consistently substituted for it. It hardly seems necessary at this time to point out that work and energy are not interchangeable terms and it is a pity to be obliged to note that this error which has caused so much confusion in the past still survives to carry that confusion into the future.

Attempts to prove by means of arithmetic and algebra something which needs the calculus always leads to a wealth of equations, but in this book algebraic equations are used with appalling profusion. It is by no means easy to retain the meanings of the various letters to the end of some of the demonstrations.

Some points are brought out with clearness and emphasis, for example

that mass and weight are not one and the same thing, that time is but relative, and that every phenomenon of nature requires some time for its occurrence.

In conclusion it must be said there is not a great deal in the book to interest the physical chemist as such, and what there is can be found in a more useful form, for his point of view at least, in other works. *S. L. Bigelow*

Electrolysis and Electrosynthesis of Organic Compounds. *By Walther Löb. Translated from the Second German Edition by H. W. F. Lorenz. 13 × 19 cm; pp. xiii and 103. New York: John Wiley and Sons, 1898. Price: cloth $1.00.* — The first German edition of this book has already been reviewed 1, 572. The English version is a translation of the second German edition. The general arrangement of the work is much the same as in the first edition. The headings for the aliphatic series are: hydroxyl compounds; ketones; acids; cyanogen compounds and compounds containing sulfur. For the aromatic compounds the chapters are: phenols; aldehydes and ketones; acids; amido-compounds; reduction and oxidation of nitro compounds; alkaloids; camphor and glucosids; electrolysis of blood and of albumen; electrolysis and electrosynthesis with alternating currents. Owing to the development of electrochemistry in the last few years, this edition contains much that was not in the first edition.

On the last page of the book the author outlines his views as to the important points to be studied during the next few years. These are: "The oxidation reactions which occur in the electrolysis of acids of the aliphatic series, the reduction reactions in the case of the aromatic series, and lastly, the reactions involving substitutions concerning which but few researches have been published". The translator has added a satisfactory name and subject index.

Wilder D. Bancroft

Les Modifications permanentes du Verre. *By L. Marchis. 16 × 25 cm; 447 pp. Paris: A. Hermann, 1898. Price: paper 10 francs.* — This book contains an application of Duhem's theory of permanent changes to the change of the zero in thermometers, assuming both a physical and a chemical hysteresis. The true reading of a thermometer is obtained only when the glass is in the state of permanent equilibrium or 'natural' state. Simply bringing a thermometer to a given temperature and holding it there is an unsatisfactory way of reaching permanent equilibrium. The best way of obtaining this result is to make the temperature oscillate between certain limits. On the first heating the volume of the glass will change in a way that can be represented by a curve, the volume and temperature being the coordinates. On the first cooling the system passes along a second curve which does not bring the thermometer back to the initial volume at the original temperature. After repeated oscillations the system at length passes through a closed cycle intersected by the curve for the natural state. By bringing the two temperatures very close together the thermometer can be brought infinitely near the 'natural' state. The author has shown experimentally that the displacement of the zero takes place much more rapidly when the temperature oscillates between perceptible limits than when the temperature is kept as nearly constant as may be. Brillouin advanced the hypothesis that the displacement of the zero in a thermometer kept for a given

length of time at a practically constant temperature was due solely to the oscillations of the temperature, while Young claimed that the time of remaining at the practically constant temperature was the sole factor to be considered. Duhem's theory and the experiments of Marchis decide conclusively in favor of Brillouin's hypothesis.

The book itself consists of an introduction, eight chapters, a conclusion and a note. The first chapter is devoted to a discussion of the thermometers, the thermostats and the plan of campaign. The second chapter consists of a "study of the permanent isobaric changes in systems depending on a single normal variable". In the third chapter we find a discussion of the effect of temperature oscillations on the displacement of the zero. Chapter four contains a general study of systems depending on two variables, each showing hysteresis, while the next two chapters are devoted to the application of the theory to special problems in thermometry. The seventh chapter deals with the possibility of chemical modifications in the glass while the best method of treating thermometers in order to obtain accurate measurements is discussed in the last chapter. In the appended note the theory is applied to explain the behavior of some of the nickel steels studied by Guillaume.

This study of thermometry is a brilliant application of Duhem's theory to a very difficult problem and the volume will appeal both to those who are interested in mathematical theory and to those who are attempting to make accurate thermometric measurements. It must be admitted however that the book is not easy reading in spite of the continual application of the theory to experimental results, and that to get real pleasure out of it calls for more enthusiasm or more mathematical training than chemists usually have.

Wilder D. Bancroft

Graham-Otto's ausführliches Lehrbuch der Chemie. *I. Band; III. Abtheilung: Beziehungen zwischen physikalischen Eigenschaften und chemischer Zusammensetzung der Körper. Third, revised, edition. Herausgegeben von H. Landolt. 15 × 23 cm; pp. xvi and 890. Braunschweig: F. Vieweg und Sohn, 1898. Price: 18 marks.*—This third, and last, part of the third volume is devoted to the relations between the physical properties and the chemical composition of substances. The first chapter on crystalline form is by Arzruni and comes down to the year 1892, the later work being condensed into some twenty pages of notes and corrections. The second chapter on volume relations is by Horstmann and comes down to about 1890. The fourth and fifth chapters on melting-points and boiling-points are by Marckwald and were finished about 1897. The chapter on refraction is by Rimbach and dates from the middle of 1897. Chapter seven on spectra was finished by G. Krüss in 1889 and notes added by H. Krüss bring it down to 1895. The chapter on optical rotation is by Landolt and is a résumé of his book on the same subject together with some additions. The last chapter on electromagnetic rotation is by Schönrock and was finished about May of 1898.

The different portions of the volume thus date from different periods and this is obvious when one reads the work. In the discussion of solid solutions, for instance, we find no mention of the phase rule and consequently we do find a statement, p. 308, that van 't Hoff's classification of mix-crystals as

homogeneous solid solutions is incomprehensible "if the internal molecular structure is meant thereby and not that which is accessible to our crude perceptions". Ostwald's explanation of the difference between monotropic and enantiotropic substances is rejected, p. 203, only too obviously because the explanation was not understood. Though in some respects this first chapter does not represent the sum total of chemical knowledge in this line, it contains a mass of interesting material well presented and will prove invaluable to the investigator, the lecturer and the student. Five out of the nine chapters bring the subjects down to the year 1897 and they are therefore free from some of the features that are open to criticism in the other portions of the book. The reviewer wishes to call especial attention to the excellence of the chapter on optical rotation, written by the editor, Landolt. The whole volume, however, is deserving of great praise and will certainly be referred to often by all who are really interested in real chemistry. *Wilder D. Bancroft*

Handbook of Metallurgy. *By Carl Schnabel. Translated by Henry Louis. Vol I.: Copper, Lead, Silver, Gold; pp. xvi and 876. Vol. II: Zinc, Cadmium, Mercury, Bismuth, Tin, Antimony, Arsenic, Nickel, Cobalt, Platinum, Aluminum; pp. xiv and 732. 16 × 23 cm. New York: The Macmillan Co., 1898. Price: cloth $10.00.*—Each chapter begins with a description of the physical and chemical properties of a metal, a brief discussion of the more important compounds, a list of the ores with reference to the localities in which these occur. After this introduction the author takes up the methods of extracting the metal from its ores. Everything is systematic and thorough. The metals are considered in the following order: copper, lead, silver, gold, zinc, cadmium, mercury, bismuth, tin, antimony, arsenic, nickel, cobalt, platinum and aluminum, the first volume being devoted to the first four metals and the second volume to the remaining eleven.

Apart from the electrolytic methods there is much to interest the physical chemist. To mention only one point, the Parkes process for desilverizing lead by means of zinc is a beautiful illustration on a large scale of Nernst's distribution law. It is interesting to note in connection with this that the metallurgists have discovered that adding aluminum or still better magnesium increases the distribution ratio. So far as the reviewer is aware no experiments have yet been made in the laboratory on the merits or demerits of 'shaking out' with mixed solvents. While the theory of the Pattinson process has long been understood, it seems quite probable that there is room for further applications of the phase rule in making more fusible slags.

The electrolytic processes are in many respects the most interesting to the theoretical chemist and it is very instructive to turn over the pages of these two volumes and note the increase in the use of electricity during the past few years, especially when we reflect that the change has only just begun. For instance, the author points out the difficulty in getting nickel to precipitate well electrolytically in any but thin layers. This has been overcome almost while the translation was in the press and the new separation of nickel from cobalt by electrolysis promises to increase the advantage of the electrolytic method almost to the exclusion of all others. From the theoretical point of

view, one is glad to see that nickel is being manufactured commercially by the 'carbonyl' process.

These two volumes are very complete and very satisfactory. It is a pleasure to note the appearance of such a work in English. The translator has done his work well and has provided an excellent index. From a scientific point of view the reviewer would have liked to have seen at least a footnote calling attention to the relative importance of current density and electromotive force in the electrolytic separation of metals. While the conditions of technical work differ very radically from those of the laboratory, it is always well, when possible, to point out the scientific basis on which the "rule of thumb" method rests. This is but a minor blemish and will undoubtedly be corrected in the next edition. The book is a distinct addition to our scientific literature.

Wilder D. Bancroft

Ostwald's Klassiker der exakten Wissenshaften. *No. 98. Ueber das Benzin und die Verbindungendesselben. By Eilhard Mitscherlich (1834). Edited by J. Wislicenus. 39 pp. 0.70 marks. No. 100. Abhandlungen über Emission und Absorption. By G. Kirchhoff (1859-1862). Edited by Max Planck. 41 pp. 1 mark. Leipzig: W. Engelmann, 1898. 12 × 19 cm.* — The first of these volumes is a reprint of an article written in 1833 and published in the Transactions of the Berlin Academy in 1835. In it Mitscherlich showed how to make benzene from benzoic acid, how to convert benzene into nitrobenzene, and into benzene sulfonic acid, how to convert nitrobenzene into azobenzene, and how to prepare benzene hexachlorid and trichlorbenzene. The paper is interesting as furnishing another instance of experiments the importance of which was not appreciated till many years later. This volume has been edited by J. Wislicenus.

The three articles collected in No. 100 are the one on the Fraunhofer lines, the one on the connection between emission and absorption of light and heat, both dating from 1859, and one on the relation between the power of emission and the power of absorption. Of these, the contents of the first are the most familiar to the general public, the consequences of the hypothesis appealing strongly to the popular fancy. The other two articles contain the natural mathematical development of the idea outlined in the first.

Wilder D. Bancroft

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry

General

The position of helium, argon and crypton in the periodic system. *W. Crookes. Zeit. anorg. Chem.* **18,** *72* (*1898*). — The author arranges the elements in a figure-eight-shaped descending spiral. At the junction of the loops occur elements that are electrically and chemically neutral. The author shows that helium, argon and crypton fit in at these points and that neon and metargon will probably do the same. *W. D. B.*

On the atomic weights of argon and helium. *H. Wilde. Comptes rendus,* **125,** *649* (*1897*). — A discussion of argon and helium with reference to the author's hypothesis in regard to the periodic law. Experiments to convert nitrogen into argon by means of an electric discharge gave negative results. *W. D. B.*

The atomic weights of nickel and cobalt. *C. Winkler. Zeit. anorg. Chem.* **17,** *236* (*1898*). — The author thinks that the values for the atomic weights of nickel and cobalt found by Richards and Cushman and by Richards and Baxter (**2,** 396) are too low owing to the presence of free hydrobromic acid in the bromids analyzed. *W. D. B.*

On the atomic weights of nitrogen, chlorin and silver. *A. Leduc. Comptes rendus,* **125,** *299* (*1897*). — Taking oxygen as 16.00 the author found 14.005 for nitrogen (**1,** 511) while Stas obtained 14.044. The discrepancy is attributed by the author to oxygen in Stas's silver and he proposes the following values: N 14.005, Cl 35.470, Ag 107.96, S 32.055, H 1.0076. *W. D. B.*

On the increasing importance of inorganic chemistry. *J. H. van't Hoff. Zeit. anorg. Chem.* **18,** *1* (*1898*). — An address delivered before the society of German scientists and physicians in Düsseldorf. *W. D. B.*

One-Component Systems

On the limits of the solid state, II. *G. Tammann. Wied. Ann.* **66,** *473* (*1898*). — Amagat's measurements on the change of the freezing-point of carbon tetrachlorid with the pressure are not satisfactory for theoretical purposes because different solid modifications occur, so that the experiments do not refer throughout to the same solid phase. Damien's measurements showing a maximum freezing-point with some substances are not trustworthy because he obtained

his pressures by pumping in air. He was thus working with a two-component system and the maximum freezing-point occurs when the lowering of the freezing-point due to the solubility of the air in the melt just counterbalances the rise of freezing-point due to the increased pressure. Demerliac's measurements are also rejected as being obviously wrong, so that there remain only the measurements of Barus on the freezing-points of naphthalene. The author has then made freezing-point determinations with various substances with pressures ranging up to 3500 kg/cm². The highest temperatures and pressures observed at which solid and liquid were in equilibrium were 81.4° and 3500 kg for benzene; 30.3° and 3500 kg for dimethyl ethyl carbinol; 93° and 3000 kg for trimethyl carbinol; 81.76° and 3146 kg for carbon tetrachlorid; 70.08° and 3265 kg for nitrobenzene; 86.2° and 1500 kg for benzophenone; 97.4° and 2000 kg for phosphorus. With trimethyl carbinol a second solid phase appears at about 60° and about 1900 kg, this being the first instance of a triple point with two solid phases and a liquid phase. With carbon tetrachlorid portions of curves were obtained for three solid modifications; but no actual intersection was verified, though it is probable that one occurs at −16° under a pressure of 100 kg/cm².

In all cases the pressure-fusion curve bends toward the pressure axis with increasing pressure. In the case of dimethyl ethyl carbinol the curvature is so marked that a temperature maximum of about 35° seems very probable. The author gives his reasons again for believing that a critical point for solid and liquid does not exist (see **2**, 58) and also expresses his disbelief in Ostwald's assumption that there is such a thing as a continuous change from solid to liquid. The experiments of Heydweiller showing the existence of a critical temperature for solid and liquid menthol have been repeated and the results are said to be due to impurities. *W. D. B.*

Reply to a comment of G. Tammann. *A. Heydweiller. Wied. Ann.* **66,** *1194 (1898).* — The author rejects Tammann's hypothesis (preceding review) that the appearance of a critical temperature for solid and liquid menthol is due to impurities. He also criticizes Tammann's proof that such a critical point is impossible. *W. D. B.*

New experiments on the liquefaction of fluorin. *H. Moissan and J. Dewar. Comptes rendus,* **125,** *505 (1897).* — Liquid fluorin liquefies readily at the boiling-point of atmospheric air. Its boiling-point is about −187° (cf. **2**, 396). It does not solidify at −210° and is miscible in all proportions with liquid oxygen and liquid air. Its density is 1.14; its surface-tension is less than that of liquid oxygen; it has no absorption spectrum and is not magnetic. At −210° it does not act on dry oxygen, on water or on mercury, but acts with incandescence on hydrogen and turpentine. *W. D. B.*

On the compressibility of gases under about atmospheric pressure. *A. Leduc and P. Sacerdote. Comptes rendus,* **125,** *297 (1897).* — Writing for each gas at any temperature the expression

$$\frac{P_0V_0}{PV} - 1 = A(P - P_0)$$

Leduc has advanced the hypothesis that the product of A into the critical pressure is the same function of the temperature for all gases (**1**, 259). In this paper it is stated that this hypothesis holds for fourteen out of eighteen gases, the exceptions being methane, methyl chlorid, ammonia and hydrogen sulfid.
W. D. B.

Densities of some easily liquefied gases. *A. Leduc. Comptes rendus*, **125**, *571* (*1897*). — The author finds 1.5287 for the density of carbonic acid; 1.5301 for nitrous oxid; 1.2692 for hydrochloric acid; 1.1895 for hydrogen sulfid; 2.491 for chlorin; 0.5971 for ammonia; and 0.2639 for sulfur dioxid.
W. D. B.

Critical constants of some gases. *A. Leduc and P. Sacerdote. Comptes rendus*, **125**, *397* (*1897*). — The critical data for hydrochloric acid are 52° and 83 atm; for PH_3 52.8° and 64 atm; for H_2S 100° and 90 atm; for $(CH_3)_2O$ 129.6° and 57 atm. The authors believe that the error in the pressures does not exceed one atmosphere nor the error in the temperatures 0.5°. *W. D. B.*

On the molecular volumes and the densities of gases in general at any temperature and under ordinary pressures. *A. Leduc. Comptes rendus*, **125**, *703*, *768* (*1897*). — Empirical formulas based on the author's experimental data (preceding reviews). *W. D. B.*

On the dissociation and polymerization of gases and vapors: the alleged dissociation of chlorin at high temperatures. *A. Leduc. Comptes rendus*, **125**, *937* (*1897*). — The author calculates the density of chlorin at different temperatures according to his formula and finds that it should be 2.4913 at 0° and 2.4483 at 1200°. The experimental determinations of Friedel and Crafts, of Jahn, of Crafts and of V. Meyer agree well with these figures and the conclusion is therefore drawn that there is no evidence of any dissociation of chlorin at any temperature. *W. D. B.*

On the isothermal and adiabatic transformations of real gases. *A. Leduc. Comptes rendus*, **125**, *1089* (*1897*). — The author has modified the usual equation for the ratio of the specific heats of a gas $pv^\gamma = const.$ into $\Delta pv^\gamma = const.$ where Δ is a factor that comes from taking the author's expression for a gas instead of the ordinary equation for ideal gases. *W. D. B.*

On aldehyde-ammonia. *M. Delépine. Comptes rendus*, **125**, *951* (*1897*). — On standing aldehyde-ammonia in a vacuum over sulfuric acid crystals are obtained to which the author assigns the formula $(CH_3.CH:NH)_3$. The new substance melts at 85° and boils at 123°–124°. Vapor-density determinations gave a molecular weight of 60.9 at 152°, of 58.4 at 182° and of 45.8 at 261°, the value for C_2H_3N being 43. Freezing-point determinations in benzene gave a value at infinite dilution of $174 = (C_2H_3N)_4$. Cryoscopic determinations of aldehyde-ammonia in water gave a molecular weight of about 162 when measured at once, and of 92–119 at the end of twenty-four hours. *W. D. B.*

Reversible transformation of styrene into metastyrene under the influence of heat. *G. Lemoine. Comptes rendus*, **125**, *530* (*1897*). — The solid metastyrene is soluble in styrene and the latter can be separated from the former by

distillation under diminished pressure. At 97° the amount of styrene per liter in the vapor phase at equilibrium is about 0.1 g, while at 310° it is about 0.7 g. Nowhere in the paper is there a clear statement of what phases are present at any time. *W. D. B.*

On the change of sulfur during heating. *F. W. Küster. Zeit. anorg. Chem.* **18,** *365 (1898).* — The amount of insoluble sulfur in a given mass of solid sulfur was determined by dissolving the soluble sulfur in carbon bisulfid and weighing the residue. The length of heating at any given temperature produced no visible effect on the amount of insoluble sulfur formed. It is also stated that the temperature has no effect on the concentration. Neither of these statements can be considered as proved although they are apparently supported by experimental data. What was established was that if sulfur be cooled slowly from a temperature of 448° it will be found to contain about two to three percent of insoluble sulfur, while it will contain over thirty percent of insoluble sulfur if the cooling be very rapid. This interesting phenomenon does not serve as a starting-point for the discussion though it is obvious that this should have been the case. *W. D. B.*

Two-Component Systems

Contributions to our knowledge of amalgams. *W. Kerp. Zeit. anorg. Chem.* **17,** *284 (1898).* — Solubility determinations have been made between 0° and 100° with sodium and mercury. The same substance $NaHg_5$ crystallizes throughout the whole range of temperatures. This compound has no true melting-point, but begins to soften at 105° and is entirely liquid at 138°. One experiment with potassium amalgam appeared to show the existence of a compound KHg_{12}; but this cannot be considered as definitely established until experiments have been made at different temperatures. With barium amalgam the amount of barium appeared to increase with rising temperature so that the existence of a solid solution is probable, though the author inclines to a belief in the compound $BaHg_{12}$. Pure sodium amalgam acts very slowly on pure sodium hydroxid. The presence of other metals causes a tempestuous evolution of hydrogen. *W. D. B.*

On the solubility of cerium sulfate in water. *W. Muthmann and H. Rölig. Zeit. anorg. Chem.* **16,** *450 (1898).* — The solubility curves have been determined for the three hydrates of cerium sulfate, those with twelve, eight and five of water. The curve for the octohydrate cuts the curve for the pentahydrate at 74° and the curve for the salt with twelve of water at 27.5°. All three hydrates show decreasing solubility with rising temperature and, according to the authors, the more soluble salt is the more stable. This is at least the third time that this phenomenon has been reported and in no one of the three cases has it struck the investigators as worthy a second thought. *W. D. B.*

On the solution pressures of some halid salts. *P. Rohland. Zeit. anorg. Chem.* **18,** *327 (1898).* — As we pass from the chlorids to the bromids and iodids of the alkalies and the alkaline earths we find increasing solubility in water and the first three alcohols, methyl, ethyl and propyl. On the other hand the iodids of mercury and copper are less soluble in these four solvents than are the chlorids. *W. D. B.*

Effect of supercooling on the freezing-points of solutions of potassium chlorid and of sugar. *F. M. Raoult. Comptes rendus*, **125**, *751* (*1897*). — The author makes use of the formula $C = C'(1 - KS)$, where C is the true freezing-point, C′ the apparent freezing-point, S the amount of supercooling and K a constant varying with the apparatus, etc. According to the author K may be calculated by means of the formula

$$K = \frac{1}{80}\left(1 + \frac{r}{R}\right) \pm \left(1 + \frac{r}{R}\right)\frac{t}{T} \cdot \frac{1}{80S},$$

where 80 is the heat of fusion of ice, r the water-worth of the wetted portion of the apparatus including the thermometer and the stirrer, R the water-worth of the cryoscopic liquid, t the time between the first appearance of solid and the thermometer's becoming stationary, T the time necessary for the apparatus to fall in temperature one degree by radiation. The second term on the right hand side of the equation expresses the effect of radiation and was negligible in the author's apparatus and the first term was equal to 0.01375, while the mean of the experimental values of K for potassium chlorid and sugar was 0.014. With potassium chlorid and with sugar the molecular lowering approached, with increasing dilution of the solution, the values required by the dissociation theory. *W. D. B.*

On the distillation of mixtures of pyridin with propionic, acetic and formic acids. *G. André. Comptes rendus*, **125**, *1187* (*1897*). — A mixture of propionic acid and pyridin, about two reacting weights of the former to one of the latter, boils constantly at 150°–151.5°, a temperature higher than the boiling-points of propionic acid and of pyridin. The author considers that there is formation of an acid salt in spite of the fact that the equilibrium is displaced towards the propionic acid side when boiling under diminished pressure.

With acetic acid and pyridin a most remarkable phenomenon was observed. A liquid containing roughly three of the acid to two of the base was found to distil constantly at 139°–140°. If this liquid were redistilled, portions of it began to pass over at 100° and the temperature rose gradually to 139°–140°. According to this, by repeated distillation of a solution having a maximum boiling-point, it is possible to separate the mixture into its components. The pitiable thing about it all is that the author sees nothing astonishing or unusual in such a statement. With formic acid and pyridin a maximum boiling-point was observed, but the statements in regard to this system are so confused that it is impossible to make anything out of them. *W. D. B.*

Boiling-point determinations of some salts in ethereal solutions. *R. Lespieau. Comptes rendus*, **125**, *1094* (*1897*). — Approximately normal values are obtained for mercuric chlorid, ferric chlorid, zinc chlorid and antimony chlorid, though with zinc chlorid the authors had to extrapolate from 230 as the last observation to 138 for complete dissociation. It is probable that the zinc chlorid contained water. With hydrated uranyl nitrate values were obtained varying from 604 to 1044. Since the formula weight of the salt including the water of crystallization is only 504, the author concludes that the salt dissolves without losing its water of crystallization because if this were not the case the molecular weight would have been lower than the calculated instead of

higher. This reasoning is bad. The splitting off of water would be more likely to lower the boiling-point than to raise it and would thus give too high values for the molecular weight. *W. D. B.*

A new procedure for determining molecular weights by the boiling-point method. *W. Landsberger. Zeit. anorg. Chem.* **17,** *422* (*1898*). — Reviewed (**2,** 400) from Ber. chem. Ges. Berlin, **31,** 458 (1898).

On some compounds of phenylhydrazin with metallic nitrates. *J. Moitessier. Comptes rendus,* **125,** *183* (*1897*). — Cobalt nitrate crystallizes with two of phenylhydrazin; zinc and cadmium nitrates with three and nickel nitrate with four of phenylhydrazin. *W. D. B.*

On some compounds of metallic acetates with phenylhydrazin. *J. Moitessier. Comptes rendus,* **125,** *611* (*1897*). — The acetates of zinc, cadmium, cobalt and manganese crystallize with two of phenylhydrazin; the acetate of nickel with three. *W. D. B.*

New compounds of phenylhydrazin with mineral salts. *J. Moitessier. Comptes rendus,* **125,** *714* (*1897*). — Nickel chlorid, nickel sulfate and cobalt bromid crystallize both with five and with two of phenylhydrazin while cobalt chlorid and cobalt sulfate crystallize both with four and with two of phenyldrazin. *W. D. B.*

On the temperature of maximum density of barium chlorid solutions. *L. C. de Coppet. Comptes rendus,* **125,** *533* (*1897*). — With 41.72 g $BaCl_2$ per kilogram of water the maximum density occurs at $-0.843°$. The lowering of the temperature of maximum density is proportional to the concentration of barium chlorid expressed in grams of salt per thousand grams of water. *W. D. B.*

Studies of salt solutions: lithium chlorid. *G. Lemoine. Comptes rendus,* **125,** *603* (*1897*). — Determinations of the specific gravities and heats of dilution of lithium chlorid in water, methyl alcohol and ethyl alcohol. *W. D. B.*

The specific gravity of sodium chloride solutions. *H. C. Hahn. Jour. Am. Chem. Soc.* **20,** *621* (*1898*). — The paper opens with the following remarkable statement: "The specific gravity and expansion by heat of salt solutions have not received the attention of chemists and physicists to the extent which they deserve. The data for common salt, for example, are only sufficient for technical purposes." As might be expected, the rest of the article is devoted to a recalculation of results published by Gerlach in 1859. *W. D. B.*

On the chlorid of parastannic acid. *R. Engel. Comptes rendus,* **125,** *464* (*1897*). — If metastannic acid be heated with boiling water a compound is obtained containing seven of water, which changes into a compound with two of water when dried in a vacuum. This new acid is called parastannic acid by the author. When treated with hydrochloric acid, it gives a solution showing Rose's reaction of precipitation with dilute sulfuric acid. *W. D. B.*

On the stannic acids. *R. Engel. Comptes rendus,* **125,** *651* (*1897*). — Metastannic acid has the composition $(SnO_2)_5 5H_2O$; stannic acid the composition $SnO_2 4H_2O$. Even in the cold stannic acid changes gradually into meta-

stannic acid, but the reaction does not run to an end. This presence of the two substances has been the cause of much of the confusion in regard to the properties of the two acids. The author believes that the equilibrium is due to the formation of a compound in which the ratio of the acids is unity. He has overlooked the possibility of a solid solution being formed. *W. D. B.*

The absorption, II. *J. M. van Bemmelen. Zeit. anorg. Chem.* **18,** *14 (1898).* — A general statement of the facts and hypotheses in regard to the behavior of colloid jellies (see **1,** 444). The formation of a jelly is due to the separation of a solution in two liquids the first of which (L_1) is colloidal, viscous and possesses a net-work structure in which the more fluid liquid (L_2) is partly absorbed and partly retained mechanically. Through different causes such as the influence of a third substance or of time or the evaporation of L_2 the colloidal liquid passes continuously into the solid state, remaining amorphous and becoming eventually like horn or glass. By the assumption of a coherent net-work of an amorphous substance the author claims that it is possible to account for all the phenomena observed with the jellies. *W. D. B.*

Poly-Component Systems

On the solubility of the bicarbonates of calcium and magnesium. *F. P. Treadwell and M. Reuter. Zeit. anorg. Chem.* **17,** *170 (1898).* — If a calcium hydroxid solution be saturated with carbonic acid and the acid in the vapor phase be then removed by air, the amount of carbonic acid retained corresponds exactly to that required for the formula of the bicarbonate. With excess of carbonic acid the solubility of the bicarbonate increases and the authors have determined this change of solubility in terms of the partial pressures and of the concentrations of free acid in the liquid phase. Although calcium bicarbonate is much more soluble in concentrated sodium chlorid solutions than in pure water, the increase is very slight when tenth-normal sodium chlorid solution is taken. Magnesium bicarbonate is not stable except in presence of an excess of carbonic acid. *W. D. B.*

Note on the chemistry of the bicarbonates of calcium and magnesium. *C. Kippenberger. Zeit. anorg. Chem.* **18,** *413 (1898).* — Attention is called to the fact that Treadwell and Reuter (preceding review) had misunderstood and misquoted some work of the author. *W. D. B.*

Correction. *F. P. Treadwell. Zeit. anorg. Chem.* **18,** *418 (1898).* — The mistakes referred to by Kippenberger (preceding review) are corrected in this note. *W. D. B.*

On some reactions in methyl alcohol and acetone. *P. Rohland. Zeit. anorg. Chem.* **18,** *322 (1898).* — Owing to the different solubilities of salts in different solvents reactions may run one way in one case and another way in a second case. In aqueous solution mercuric iodid precipitates and potassium chlorid goes into solution. In acetone potassium chlorid precipitates, leaving mercuric iodid in solution. Cadmium iodid precipitates from an aqueous solution of cadmium bromid and potassium iodid, while potassium bromid separates from a solution in acetone. Mercuric iodid will not precipitate cuprous iodid from a solution of a cupric and a ferrous salt in methyl alcohol. The reaction

between potassium bichromate and silver nitrate takes place more slowly in methyl alcohol than in water. The reaction between barium chlorid and potassium bichromate takes place very slowly in methyl alcohol, but this is probably due to the absence of the water required for the reaction. *W. D. B.*

Conversion of potassium iodid and bromid into chlorid. *F. W. Küster. Zeit. anorg. Chem.* **18,** *77 (1898).* — By passing a current of chlorin over potassium iodid heated in a porcelain crucible, it is possible to convert the iodid completely into chlorid without any difficulty and at a very moderate temperature. The conversion of the bromid could not be effected in this way without loss of substance because the necessary temperature was so high that some of the potassium chlorid volatilized. On placing the potassium bromid in an Erlenmeyer flask, moistening with water and then passing in chlorid complete conversion was obtained without difficulty. The results in the two cases are very accurate because there is no precipitation, filtration or anything of that kind.

W. D. B.

On the behavior of some salts of chlorplatinic acid. *P. Rohland. Zeit. anorg. Chem.* **15,** *412 (1897); 16, 305 (1898).* — Crystallized barium chlorid is fairly soluble in methyl alcohol and very insoluble in ethyl alcohol. While magnesium and calcium chlorplatinates dissolve in ethyl alcohol without decomposition, barium chlorplatinate is decomposed into insoluble barium chlorid and soluble platinic chlorid. We have thus an instance of a substance that is a complex salt in water and a double salt in alcohol. Sodium chlorplatinate behaves in the same way. With methyl alcohol the phenomena are much less marked owing to the greater solvent action of the methyl alcohol for the alkaline halids. *W. D. B.*

On the solubility of liquids. *A. Aignan and E. Dugas. Comptes rendus,* **125,** *498 (1897).* — The authors have determined the temperatures at which different mixtures of benzene and hydrated acetic acid form two liquid phases. They consider that up to fifty percent of acetic acid the benzene is solvent and that the acid is solvent for higher concentrations. They also believe that there are two solubility curves forming a cusp. *W. D. B.*

On the accidental causes of irreversibility in chemical reactions. *A. Colson. Comptes rendus,* **125,** *945 (1897).* — The reaction $Ag_2S + H_2SO_4 = Ag_2SO_4 + H_2S$ is not reversible because a second reaction thereupon takes place represented by the equation $H_2S + 3H_2SO_4 = 4H_2SO_3$. The action of hydrochloric acid gas on normal phosphates is also not reversible in the ordinary sense because of the secondary formation of pyrophosphates. *W. D. B.*

The action of nitric acid on tin. *R. Engel. Comptes rendus,* **125,** *709 (1897).* — Ordinary nitric acid diluted with not less than twice its volume of water acts on tin forming stannous nitrate. Diluted with one volume of water it attacks tin forming stannic nitrate. Ordinary nitric acid attacks tin forming stannic nitrate insoluble in an acid of this concentration. Stannic nitrate changes readily in dilute acid or at higher temperatures to stannic acid, traces only of metastannic acid being formed. Stannic acid changes slowly and partially into metastannic acid while, in boiling water, metastannic acid changes

into parastannic acid, which last is considered by the author as an internal anhydrid of metastannic acid. *W. D. B.*

Researches on the state in which elements other than carbon are found in cast iron and in steel. *A. Carnot and Goutal. Comptes rendus*, **125**, *148, 213 (1897)*. — In ferrosilicon most of the silicon is present as FeSi, though compounds are also formed containing relatively more iron. When manganese is present it combines with the silicon. No formula is given for the compound thus formed owing to the difficulty of separating it from the FeSi. When cast iron contains both manganese and sulfur, it is believed that MnS is formed in preference to FeS. Phosphorus, on the other hand, combines with the iron forming Fe_3P, rather than with the manganese. Arsenic does not combine with iron at all. The same is true of copper, nickel, titanium and probably of manganese. Chromium forms carbids of chromium and iron, while tungsten forms the compound Fe_3Mo and molybdenum the compound Fe_2Mo_3.
W. D. B.

On the formation of mixed hydrates of acetylene and some other gases. *De Forcrand and Sully Thomas. Comptes rendus*, **125**, *109 (1897)*. — Acetylene and water can be made to unite at about 0° with CCl_4, $CHCl_3$, $C_2H_4Cl_2$, CH_3I, $CHBr_3$ or other halogen compounds forming crystals containing all three components. On decreasing the pressure or raising the temperature these mixed hydrates effloresce giving off acetylene. *W. D. B.*

On different double chlorids formed with cinchonamin. *L. Boutroux and P. Genvresse. Comptes rendus*, **125**, *467 (1897)*. — The chlorids of cadmium, zinc and copper can crystallize with two of cinchonamin hydrochlorid.
W. D. B.

The triple nitrites of some metals. *C. Przibylla. Zeit. anorg. Chem.* **15**, *419 (1897)*; **18**, *448 (1898)*. — In the first paper the author shows that while some triple nitrites can be obtained giving results agreeing well with the general formula $R(NO_2)_2.R(NO_2)_2.2RNO_2$, the majority of the substances do not correspond to any definite formula. In the second paper it is shown that solid solutions are formed with the nitrites of Cu, Sr and K; Cu, Sr and NH_4; Cu, Ca and K; Ni, Sr and K; Cu, Pb and Tl. *W. D. B.*

Preparation of ammonium and potassium bromoplatinates. *G. Měker. Comptes rendus*, **125**, *1029 (1897)*. — At 250°–350° platinum is not attacked appreciably by either ammonium bromid or ammonium sulfate, while a mixture of the two salts attacks it readily forming ammonium bromoplatinate. On replacing the ammonium sulfate by potassium bisulfate, potassium bromoplatinate is formed, but the yield is much less good. *W. D. B.*

Process of separation and distillation of bromin from a mixture of alkaline bromids and chlorids. *H. Baubigny and P. Rivals. Comptes rendus*, **125**, *527 (1897)*. — After decomposing the bromids with copper sulfate and potassium permanganate the authors volatilize the bromin by means of an air current and pass it into a dilute solution of caustic soda. *W. D. B.*

Separation and direct titration of the chlorin and bromin in a mixture of salts of the alkaline metals. *H. Baubigny and P. Rivals. Comptes rendus,* **125,** *607 (1897).* — The method is that described in the preceding review. The amount of bromin that does not volatilize decreases with increasing concentration of the copper sulfate. On the other hand chlorin passes over if the concentrations of the sulfate and the permanganate increases too much. Directions are given for avoiding both these evils. *W. D. B.*

Use of fluorescein to detect traces of bromin in a salt solution. *H. Baubigny. Comptes rendus,* **125,** *654 (1897).* — In order to detect whether all the bromin has been volatilized (preceding two reviews) the author tests the solution with paper that has been plunged in a fluorescein solution. If bromin is present eosin is formed which is recognized by the color. One milligram of potassium bromid suffices for a marked test. *W. D. B.*

On the cuprosammonium bromids and the cuprammonium sulfocyanates. *T. W. Richards and B. S. Merigold. Zeit. anorg. Chem.* **17,** *245 (1898).* — A study of some inorganic compounds from no definite point of view under no definite conditions and leading to no definite results. *W. D. B.*

On a point in the theory of dyeing. *L. Vignon. Comptes rendus,* **125,** *357 (1897).* — The author has measured the amount of absorption when a given weight of cotton is placed for fifteen minutes at 100° in neutral and alkaline baths of different nitrogen bases. Since the concentrations were not varied, the only result of this investigation is that the different bases are absorbed to different extents under the conditions of the experiments. *W. D. B.*

On the first stages of the combination between hydrogen and oxygen. *M. Berthelot. Comptes rendus,* **125,** *171 (1897).* — On heating mixtures of hydrogen and oxygen in glass tubes at 280°, amounts of water varying from five to thirteen percent were formed. In presence of barium oxid there was no reaction at 180°, but combination begins to take place at 250°. At 280° 89.2 percent of the gases had combined in five hours and the reaction was complete in twenty-six hours. The course of the reaction appears to be formation of water and of barium peroxid leaving hydrogen; the hydrogen then reduces the peroxid forming more water. Caustic potash accelerates the reaction, the glass being attacked and a manganate being formed in one case from the manganese in the glass. *W. D. B.*

Influence of dehydrating agents on the combination of hydrogen and oxygen. *M. Berthelot. Comptes rendus,* **125,** *675 (1897).* — The presence of hydrochloric acid has no perceptible influence on the combination of hydrogen and oxygen either at 100° or at 280°. Boron trifluorid appears to hinder the reaction somewhat; but the change is probably due to a change in the surface of the glass vessel due to the boron trifluorid rather than to any direct action of this substance on the gaseous mixture. At 100° SO_2 has no effect; at 280° the SO_2 appears to attack the oxygen leaving the hydrogen intact. Liquid sulfuric acid is reduced by hydrogen at 280° and does not cause the hydrogen to react with the oxygen. Phosphorus pentoxid appears also to have no accelerating effect. *W. D. B.*

Action of hydrogen on sulfuric acid. *M. Berthelot. Comptes rendus,* **125,** *743 (1897).* — At 250° the reaction between sulfuric acid and hydrogen runs to an end, the products being water and sulfur dioxid. When oxygen is present it oxidizes the sulfur dioxid. *W. D. B.*

Influence of oxygen on the decomposition of the hydracids by metals and especially by mercury. *M. Berthelot. Comptes rendus,* **125,** *746 (1897).* — Pure hydrochloric acid and pure hydrogen sulfid do not attack mercury in the cold; but do in the presence of oxygen. A thermochemical explanation is given for this phenomenon. *W. D. B.*

On the action of some gases and metals on the photographic plate. *B. v. Lengyel. Wied. Ann.* **66,** *1162 (1898).* — Hydrogen, carbon monoxid and ethylene change the silver bromid of a photographic plate in such a way that it can be reduced by a developer. Oxygen, carbonic acid and nitric oxid have no such effect. Zinc in dry air freed from carbonic acid has no effect on the plate while in an atmosphere containing moisture and carbonic acid an intense action takes place. From this experiment the author concludes that the reported action of metals on photographic films is due to the hydrogen evolved during the corrosion of the metal. Special experiments showed that there was no such absorption of hydrogen as would be required on the hypothesis that the latent picture is due to the formation of Ag_2Br. *W. D. B.*

Electromotive Forces

Studies on the constitution of lead salts in aqueous solutions. *H. F. Fernau. Zeit. anorg. Chem.* **17,** *327 (1898).* — The author has determined the freezing-points and saturation-points of solutions containing lead salts with and without other salts. He has also determined the electromotive force of concentration cells containing lead salts and has studied the effect of the oxygen electrode on solutions of lead nitrate. As a result of these determinations the author concludes that, in addition to the electrolytic dissociation of lead chlorid into $\overset{+\,+}{Pb}$ and $\overline{\overline{Cl}}$ as ions, it is necessary to assume hydrolytic dissociation. For very dilute solutions the following equation is suggested:

$$100PbCl_2 + 63HOH = 10\overset{+\,+}{Pb} + 92\overline{\overline{Cl}} + 27PbCl_4 + 63PbO_2H_2 + 126\overset{+}{H}.$$

Lead hydroxid by itself dissociates into $\overset{+\,+}{Pb}$ and $2\overline{OH}$; but this is hardly an important factor in lead chlorid solutions owing to the presence of hydrogen as ion. *W. D. B.*

On the contact electricity between metals and liquids. *A. Heydweiller. Wied. Ann.* **66,** *535 (1898).* — An attempt to apply Coehn's law (**2,** 520) to the potential difference between metals and liquids. In many instances this was successful; but gold and platinum in methyl alcohol, ethyl alcohol, amyl alcohol and amyl acetate are exceptions as is also gold in benzene. In the arrangement Pt | amyl alcohol | amyl acetate | Zn the zinc is cathode. *W. D. B.*

On the charging of dielectrics. *A. Coehn Wied. Ann.* **66,** *1191 (1898).* — Commenting on the paper of Heydweiller (preceding review) the author points

out that in his first paper (**2**, 520) he explicitly excluded metals from the discussion. The metals are to be considered in a later paper and attention is called to the fact that Heydweiller's experiments (preceding review) are inconclusive because he has forgotten to consider oxidation as a possible disturbing element. *W. D. B.*

On the phenomenon of the electric arc. *A. Blondel. Comptes rendus*, **125**, *164* (*1897*). — The author considers that the electric arc is to be treated as a resistance. He considers that the counter electromotive force cannot exceed 0.15 volt and that therefore no electrolytic action takes place. [Cf. **2**, 207.]
W. D. B.

On the direct transformation of heat into electrical energy. *M. Deprez. Comptes rendus*, **125**, *511* (*1897*).—An alloy of nickel and iron containing thirty percent of nickel is very magnetic at 50° and loses this property at 104°. By altering this alloy between these two temperatures the author proposes to generate an alternating current. *W. D. B.*

Electrolysis and Electrolytic Dissociation

On the electrolysis of hydrochloric acid. *F. Haber and S. Grinberg. Zeit. anorg. Chem.* **16**, *198*, *329* (*1898*.)—The first of these two papers is devoted to the theory and practice of the electrolysis of aqueous hydrochloric acid at ordinary temperatures with smooth electrodes. Chlorin as ion has a lower decomposition voltage for the same concentration than hydroxyl as ion. The concentration of hydroxyl as ion is restored continually by the dissociation of water while the concentration of chlorin as ion can only be renewed by the diffusion, electrolytic and otherwise, of hydrochloric acid. With increasing current density there will therefore be an increasing percentage of hydroxyl discharged. Since the dissociation of water does not take place instantaneously, the effect of increasing current density will also be to decrease the concentration of hydroxyl as ion and, according to the authors, the curves showing the relation between concentration of acid and percentage discharge of hydroxyl as ion for different current densities will intersect. The actual case is not so simple as the one here imagined because there is the possible formation of hypochlorous, chloric and perchloric acids to be considered. As a matter of fact the authors succeeded in showing the existence of a point of intersection.

The experimental study of the yields of the different substances gave the following results. With concentrated solutions of hydrochloric acid a 100 percent yield of chlorin is obtained at the anode, dropping nearly to zero with dilute acid. Traces of hypochlorous acid are formed in the electrolysis of dilute solutions. About one-third of the theoretical amount of perchloric acid is obtained during the electrolysis of solutions varying from normal to thirtieth-normal. Simultaneously with the chloric acid there are formed small quantities of hydrogen peroxid. With very dilute hydrochloric acid solutions perchloric acid is formed, the yield being about one-fourth the theoretical. With dilute solutions much oxygen is evolved.

In the second paper the authors consider the effect of the presence of other compounds in the aqueous hydrochloric acid, the effect of temperature and of

platinized electrodes. With bases or metallic salts present in the solution, the transference numbers vary and therefore the rate at which chlorin as ion diffuses to the anode. When the solution is alkaline a large part of the current is carried by hydroxyl as ion and there is also the tendency of chlorin to react with the alkali forming sodium hypochlorite while the action of hypochlorous acid or hydrochloric acid becomes practically zero. It is thus clear that relatively more oxygen will be evolved from alkaline than from acid solutions. Oettel considered the rise of temperature as equivalent to an increase in alkalinity. The authors prefer the statement that less oxygen reacts with the hydrochloric acid. Platinizing the electrodes causes a marked increase in the evolution of oxygen.

W. D. B.

The electrolysis of hydrochloric acid with remarks on the cathodic formation of lead. *F. Haber. Zeit. anorg. Chem.* **16,** *438 (1898).* — A discussion of the conditions under which a platinum anode is attacked by chlorin, with special reference to the Nernst theory. The author postulates that platinum will go into solution so long as the potential difference is greater when we consider the electrode as a platinum electrode than when we consider it as a chlorin electrode. From this it appears to follow that the more concentrated the acid the less the platinum would be attacked which is absurd. Since platinum is present in the solution of a chlorid as part of a chlorplatinate ion, the dissociation of the chlorplatinate into platinum and chlorin as ions is forced back by the presence of chlorin as ion and therefore increasing the concentration of the acid decreases the concentration of platinum as ion more rapidly than it increases the concentration of chlorin as ion, thus making the platinum more readily attacked in concentrated than in dilute solutions. This is very ingenious and apparently all right, granting the premises; but one cannot help feeling what a fortunate thing it is that platinum should form a part of the anion in chlorid solutions. One wonders also whether any metal or any acid will ever be found — barring passive states — for which increasing the acid will make the metal less readily attacked. The question becomes even more interesting when we read that the concentration of platinum as ion must decrease with rising temperature "because platinum is more readily attacked by hot acid than by cold".

Attention is called to the fact that the evolution of hydrogen at a platinum cathode causes the electrode to disintegrate mechanically. Substituting lead for platinum the author has succeeded in forming a thin layer of spongy lead.

W. D. B.

On electrolytic formation of hydrogen peroxid. *F. Haber and S. Grinberg. Zeit. anorg. Chem.* **18,** *37 (1898).* — A discussion of the question whether hydrogen peroxid can be formed at the anode by direct union of two of hydroxyl as ion, accompanied by measurements of the potential of platinum and gold in different concentrations of aqueous hydrogen peroxid. The reaction probably does not take place because it was shown that hydrogen peroxid and oxygen cannot coexist in presence of platinum. The formation of hydrogen peroxid during the electrolysis of hydrochloric acid noticed by the authors (two reviews back), proves, on further investigation, to take place during the filtration and thus is not a product of electrolysis at all. In the experiments re-

ferred to the solution at the anode was shaken up with mercury and filtered. The finely divided mercury remained on the filter paper and oxidized with formation of hydrogen peroxid if exposed to the air. *W. D. B.*

On the electrolytic separation of nickel and cobalt from iron. *O. Ducru. Comptes rendus*, **125**, *436* (*1897*). — The solution containing nickel and iron is evaporated to dryness with a slight excess of sulfuric acid. Water, ammonium sulfate, and concentrated ammonia are added and the resulting solution electrolyzed. Presence of chromates prevents the precipitation of nickel.
W. D. B.

The quantitative determination of manganese and the separation of iron from manganese by electrolysis. *F. Kaeppel. Zeit. anorg. Chem.* **16**, *268* (*1898*). — On electrolyzing a solution of manganese sulfate to which acetone has been added, the manganese peroxid precipitates as a coherent film. As much as 1.6 g MnO_2 has been precipitated in this way, much more than has been possible by any other method (Cf. **1**, 453). The peroxid can be dried at 100°–150° and weighed as such, thus avoiding the evils due to igniting.

To separate iron from manganese the author pours the solution containing the sulfates of two metals into a boiling solution of sodium pyrophosphate, adds a few drops of phosphoric acid and electrolyzes cold. Most of the iron is precipitated as metal at the cathode, but a little separates with the manganese peroxid so that the method gives results accurate only to within one percent.
W. D. B.

On the electrolytic conductivity of trichloracetic acid. *P. Rivals. Comptes rendus*, **125**, *574* (*1897*). — The author finds that the change of the molecular conductivity of trichloracetic acid with the volume is proportional to the change of the heat of dilution with the volume. *W. D. B.*

Addition to the article: Dissolving platinum and gold in electrolytes. *M. Margules. Wied. Ann.* **66**, *540* (*1898*). — In this addition to the original paper (**2**, 516) the author points out that excellent results can be obtained by means of a rotating commutator so arranged that at one moment the battery current passes through the cell and at the next the cell is short-circuited. The belief is expressed that the periodic depolarization is the essential feature in causing the platinum and gold to dissolve. *W. D. B.*

Relation between the polymerization of liquids and their power of dissociating electrolytes. *P. Dutoit and E. Aston. Comptes rendus*, **125**, *240* (*1897*). — Conductivity measurements have been made with ammonium sulfocyanate, mercuric chlorid, silver nitrate, sodium bromid, lithium salicylate, cadmium iodid and cadmium bromid in propionitrile; with cadmium iodid and sodium salicylate in acetone; with mercuric chlorid, ammonium sulfocyanate, sodium salicylate and cadmium iodid in methyl ethyl ketone; with ammonium sulfocyanate, cadmium iodid, and sodium salicylate in methyl propyl ketone. These solvents were selected as having abnormal capillary constants, and since molecular conductivities were obtained varying from 3 in some cases to 38 in others, the authors believe themselves justified in postulating a relation between the polymerization and the dissociating power of the solvent. *W. D. B.*

SOLID SOLUTIONS

BY HAMILTON P. CADY

No complete freezing-point curves have hitherto been determined for systems in which two series of solids solutions occur. Owing to the ease of analysis naphthalene and monochloracetic acid[1] seemed a good system to investigate. The naphthalene used in these experiments was purified by repeated crystallization from aqueous alcohol and melted sharply at 79.9°. The monochloracetic acid was purified by fractional distillation. It boiled at about 185° and melted at 62°. The following method was used in preparing and separating the solid solutions. By preliminary experiments it was determined what amounts of acid and naphthalene should be taken in order to get suitable amounts of the solid and liquid phases at each temperature. A mixture of acid and naphthalene was then melted and placed in the apparatus shown in Fig. 1.

In the diagram, A is a funnel which held the melted mixture and in which the crystallization took place; C is a stirrer; D is a glass stopper for closing the bottom of the funnel until it was time to draw off the liquid; E is an asbestos filter; F a glass tube sealed to the stem of the funnel so that this latter can be kept warm to the very tip; H a tube containing soda-lime. The whole apparatus was jacketed with a water-jacket B kept at a constant temperature by the method previously described.[2] The solution was kept for several hours at the desired temperature and stirred frequently. At the end of the experiment the liquid portion was sucked off by means of a filter pump. The

[1] Some unpublished measurements made in Leipzig by Mr. Buckingham seven years ago had made it probable that these two substances formed two series of solid solutions.

[2] Jour. Phys. Chem. **2**, 242 (1898).

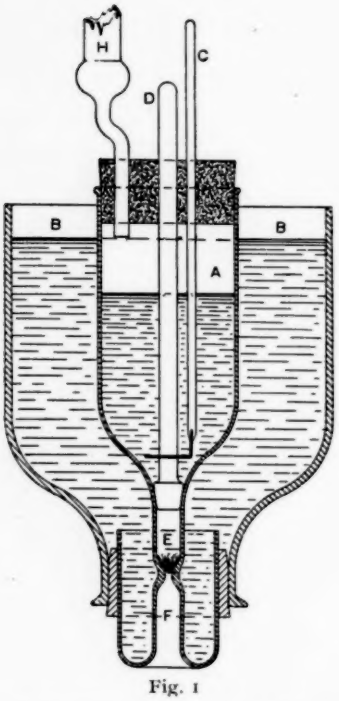


Fig. 1

temperature was then raised until the solid solution liquefied and the melt was filtered off. The two filtrates were analyzed by taking weighed portions and titrating the acid with potassium hydroxid solution. The naphthalene was determined by difference. There was no difficulty in dissolving the acid out of the naphthalene by means of water. On shaking the solid mass with water hot enough to melt it, the acid went into solution in a very short time. If the crystals were finely pulverized, cold water would remove all the acid very quickly. In fact no difference could be detected qualitatively between the rate at which the acid dissolves from a finely powdered solid solution of naphthalene and monochloracetic acid and that at which it dissolves from a mechanical mixture of the same two substances. In this

respect these solid solutions differ markedly from those in which barium sulfate is one of the components. In spite of the solubility of barium chlorid in water, it can only be washed out with incredible slowness from precipitated barium sulfate. In separating monochloracetic acid from naphthalene, it is advisable not to use hot water any more than is absolutely necessary, otherwise there will be a secondary reaction forming glycolic and hydrochloric acids.

The analytical results expressed in grams per hundred of the two components are given in Table I, the data for the fusion curve along which the crystals are chiefly naphthalene being given under the heading of 'naphthalene series', while the data for the other fusion curve are given under 'acid series'.

TABLE I

Naphthalene series

Temp	Solid solution Naph	Solid solution Acid	Liquid solution Naph	Liquid solution Acid
75°	96.6	3.4	84.4	15.6
70	95.4	4.6	69.7	32.3
65	89.2	10.8	53.3	46.7
60	80.3	19.7	42.4	57.6
55	59.6	40.4	31.3	68.7
53.5	...	...	29.4	70.0
		Acid series		
60°	1.7	98.3	4.0	96.0
55	2.1	97.9	21.0	79.0

These results are shown graphically in Fig. 2. AC and BC give the compositions of the saturated solutions. AD gives the compositions of the solid solutions containing an excess of naphthalene and BE the compositions of the crystals. By the ordinary method it is of course impossible to determine the composition of the solid phases at the quadruple point because a mixture of the two phases separates. The temperature at this point is 53° and the liquid solution contains 71.3 percent acid to 28.7 percent naphthalene. The curve BE is so nearly a straight line that no serious error will be made by extrapolating

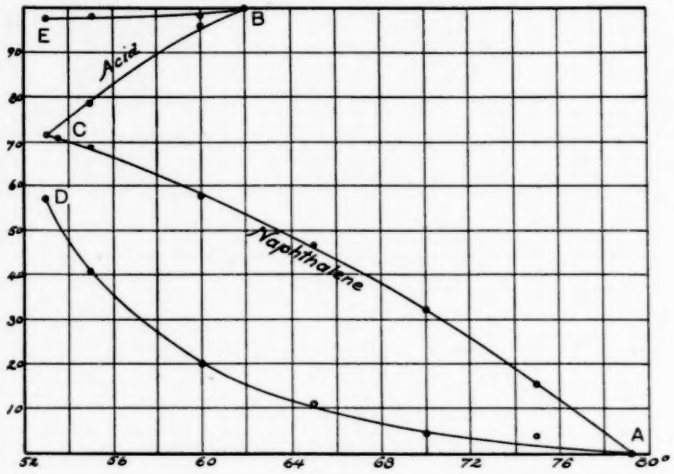


Fig. 2

and taking the composition of the crystals as 97.5 percent acid and 2.5 percent naphthalene. On the other hand the curvature of AD is such that an extrapolation from 55° to 53° is not necessarily very accurate. An attempt was therefore made to determine the limiting composition by the following method. Different mixtures of naphthalene and acid were allowed to solidify and then examined under the microscope. When the mixture contained fifty percent of acid or less there was only one kind of crystal. With sixty percent of acid two kinds of crystals could be detected. We may therefore consider 57 percent of acid as being very near the truth.

It was thought possible that acetic acid might also form solid solutions with naphthalene, but a few experiments showed that this was not the case and that the two substances crystallize without admixture. No experiments were made with monobromacetic acid because it seemed reasonably certain that this substance would behave like monochloracetic acid. On the other hand it seemed of interest to make some qualitative experiments with glycolic acid to determine whether the replace-

ment of hydrogen by hydroxyl would tend to make solid solutions possible. The glycolic acid was made from monochloracetic acid and was not entirely free from water. In spite of the traces of moisture very considerable quantities of acid dissolved in the solid naphthalene. At 74.5° the solid phase contained 18.7 percent acid as against 3.38 percent monochloracetic acid at 75° or 4.61 percent at 70°. Experiments were also made with malonic and succinic acids; but these acids are so sparingly soluble in melted naphthalene that there was practically no lowering of the freezing-point and it was impossible to make measurements. We may conclude therefore that malonic and succinic acids do not form solid solutions with naphthalene.

It was noticed that the glycolic acid could not be washed out readily from the naphthalene; it being necessary to melt the latter in order to effect a separation. In this respect it resembles the solid solutions formed with barium chlorid and barium sulfate.

Since the time of van 't Hoff's paper on solid solutions[1] it has been clear that the solute lowers the vapor-pressure of the solid solvent; but there have been reasons for supposing that the relation between concentration and lowering of the vapor-pressure was not the same quantitatively for the solid and for the liquid solutions. Küster[2] pointed out that, according to the theory, the freezing-point should remain unchanged when the solid and liquid solutions had the same composition. This, however, is not the case for many isomorphous mixtures and for this reason Küster proposed to classify isomorphous mixtures as something different from solid solutions. Walker and Appleyard[3] found that the reacting weight of picric acid in silk as determined by applying Nernst's distribution law to the system, silk, water and picric acid, was less than the reacting weight in water. This struck them as so improbable that they decided that picric acid and benzene did not form a solid solution. Küster[4] obtained even more surprising results with the system, iodin, starch and

[1] Zeit. phys. Chem. **5,** 322 (1890). [2] Ibid. **12,** 510 (1893).
[3] Jour. Chem. Soc. **69,** 1334 (1896). [4] Liebig's Annalen, **283,** 360 (1894).

water, the apparent reacting weight of the iodin in the starch being only one-fifth of the value in water. There seems no good reason for denying the existence of solid solutions in all three of these cases. By definition a solid solution is a solid phase whose composition can vary continuously within certain limits.[1] Isomorphous mixtures certainly come under this head. To make a qualitative classification on the basis of the applicability or non-applicability of a quantitative theorem such as the van 't Hoff–Raoult formula is putting the cart before the horse. The distinctions made by Küster and by Walker and Appleyard are also bad in that the phases which are cast out of the ranks of the solid solutions are not taken in anywhere else and remain as waifs and strays. The only conclusion which does not go beyond the facts is that in certain cases of solid solutions that have been examined, the van 't Hoff–Raoult formula for the change of the partial pressure with the concentration does not hold — as usually applied. The next step is to try to find out what the disturbing factor is.

For isomorphous mixtures we know that the formula, as usually applied, does not hold. It is not known whether it applies in the case of systems where two series of solid solutions are possible. Owing to the low vapor-pressures of such systems, direct measurements present very unusual difficulties. It is possible in some cases to obtain an approximate result by an indirect method. The effect of the separation of a solid solution is to raise the apparent freezing-point of the liquid solution. In case a solid solution does not separate the lowering of the freezing-point can be calculated approximately by means of the formula $K_1\Delta T = \frac{n}{N+n}$. The difference between this calculated freezing-point and the actual freezing-point gives the rise of freezing-point due to the solid solution. According to the van 't Hoff formula, as ordinarily applied, the same formula that had been used to calculate the lowering of the freezing-point should

[1] Bodländer has written an excellent statement of our knowledge in regard to solid solutions. Jahrbuch für Mineralogie, Geologie und Palaeontologie. Beilage-Band, **12**, 52 (1898).

describe the relation between the rise of freezing-point and the concentration of the solid solution. It is clear that this method is not very accurate. It assumes that the lowering of the freezing-point can be calculated with accuracy in case no solid solutions occur. This is not strictly true for any solutions over any considerable range of temperature and does not hold at all for many solutions, such as alcohols or oximes in benzene. The assumption is also made that the reacting weight is 'normal' in the two solutions and there is the further assumption that the heat of fusion is unchanged. Then, too, the rise of freezing-point is the difference between two other values and contains a relatively large percentage error. For this reason the results by this method can never be very satisfactory, though they may be instructive.

The observations with naphthalene and monochloracetic acid have been calculated on this basis, as being the only data available. If ΔT is the depression of the freezing-point calculated on the assumption of no solid solution, and $\Delta T'$ is the observed lowering of the freezing-point, the rise $\Delta T''$ due to the solid solution will be given by the equation $\Delta T - \Delta T' = \Delta T''$.[1] The results of the calculations for the naphthalene series are given in Table II. The constant used in calculating ΔT was 0.0183, and the K in the fifth column is that calculated, taking $\Delta T''$ and the concentrations in the solid phase as given.

TABLE II

Naphthalene series

Temp	ΔT	$\Delta T'$	$\Delta T''$	K_1
75°	10.9°	4.9°	6.0	0.0075
70	20.0	9.9	10.1	0.0061
65	29.8	14.0	14.9	0.0095
60	35.8	19.9	15.9	0.0157
55	40.8	24.9	15.9	0.0300

It will be noticed that K_1 is in no sense of the word a constant; but it would be unsafe to draw the conclusion that the van 't Hoff-Raoult formula did not apply to the solid solutions of monochloracetic acid in naphthalene. The range of temperatures

is nearly twenty-five degrees and it is doubtful whether the formula would apply to any system under such circumstances. Acetic acid gives abnormal results in benzene and presumably in naphthalene and there is no reason to suppose that monochloracetic acid does not do the same. For this reason the calculated values for ΔT are unquestionably too large and the same is true for $\Delta T''$. Decreasing $\Delta T''$ would make the values of K diverge more than they now do; but, on the other hand, if we are to assume polymerization in the liquid solution there is certainly no reason why a similar state of things should not occur in the solid phase. It must be admitted that this is an exceptionally bad case from which to make deductions and that the most one is justified in saying is that it has not been possible to confirm the van 't Hoff–Raoult formula.

The results with the acid series are equally unsatisfactory. The value of the constant was 0.0173, the heat of fusion being taken from Pickering's data.[1] For the first observation the actual lowering of the freezing-point is slightly greater than that calculated on the assumption of no solid solution, a result doubtless due to experimental error. For the other observation the rise of the freezing-point $\Delta T''$ is roughly twice what it should be. In the first three observations in Table II the values for K_1 are not over half what they should be, meaning that the rise of freezing-point as calculated is not less than twice as great as that required by the theory. If we try to account for this by assuming that the error is in ΔT, we are placed in the unpleasant position of having to assume very considerable polymerization in the liquid phase in order to get 'normal' results in the solid phase. In view of the fact that in all cases of isomorphous mixtures the rise of the freezing-point is greater than that required by the formula, it is probable that one may make the generalization that in solid solutions the lowering of the partial pressure is always greater than could be predicted from the van 't Hoff-Raoult formula in its usual form. To assume dissociation in order to account for this would be ridiculous.

[1] Jour. Chem. Soc. **67**, 664 (1895).

Although it is not possible at present to treat the subject quantitatively, for lack of sufficient data, it is easy to show qualitatively that the van 't Hoff-Raoult formula could not be expected to apply to solid solutions save in very exceptional cases. The deduction of the formula $\frac{n}{N} = \log \frac{p}{p_1}$ is the same for a solid as for a liquid solution and contains the explicit assumption that the heat of dilution is zero. In the case of liquid solutions the heat of dilution may be so great as to reduce the apparent molecular weight nearly to half the normal value, as for instance with the amalgams of the metals of the alkalies and of the alkaline earths.[1] We know nothing about the heat of dilution of solid solutions; but there is no reason to suppose that it is zero in the large majority of cases. Whenever it is not zero the formula of van 't Hoff-Raoult for the change of partial pressure with concentration will not apply unless a correction be applied for the heat of dilution. Another factor that has been completely disregarded by Küster and others is that the heat of fusion of the solid solution is not that of either pure component. We see therefore that there is no reason why the change of pressure with concentration in solid solutions should follow the simple van 't Hoff-Raoult formula. It is also obvious that all determinations of reacting weights in solid solutions are liable to very considerable errors, errors of such extent as practically to vitiate all conclusions drawn from them — for the present.

This research has been carried on under the direction of Professor Bancroft. The chief results are:

1. Naphthalene and monochloracetic acid form two series of solid solutions.

2. The data necessary for the construction of the concentration-temperature diagram have been determined.

3. Glycolic acid forms two series of solid solutions with naphthalene and is much more soluble in naphthalene than is monochloracetic acid.

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[1] Ramsay. Jour. Chem. Soc. **56**, 521 (1889). Cf. Cady. Jour. Phys. Chem. **2**, 525 (1898).

4. Acetic acid does not form solid solutions with naphthalene and it is probable that malonic and succinic acids do not.

5. It is probable that for most solid solutions $\frac{n}{N} < \log \frac{p}{p_1}$.

6. The cause of this discrepancy is to be sought in the heat effects.

Cornell University

A DEMONSTRATION OF THE PHASE RULE

BY PAUL SAUREL

The various demonstrations of the phase rule in existence are open to one of two objections: they are either long or incomplete. The object of the present note is to give a demonstration which shall be both short and complete.

Let r be the number of phases in a heterogeneous mass, and n the number of its independent components. If the energy, entropy, volume, temperature, pressure, and masses of the components, of the unit of mass of the i-th phase be denoted by $\epsilon_i, \eta_i, v_i, t_i, p_i, m_{i1}, m_{i2}, \ldots, m_{in}$ (so that m_{ij} denotes the mass of the j-th component which is contained in the unit of mass of the i-th phase) it can be shown[1] that

$$d\epsilon_i = t_i d\eta_i - p_i dv_i + \mu_{i1} dm_{i1} + \mu_{i2} dm_{i2} + \cdots + \mu_{in} dm_{in}, \qquad (1)$$

in which the m's are not independent but are connected by the equation

$$m_{i1} + m_{i2} + \cdots + m_{in} = 1. \qquad (2)$$

ϵ_i, t_i, p_i, and the μ's are functions of η_i, v_i and the m's, and consequently η_i, v_i can be expressed in terms of t_i, p_i and the m's; we may therefore say that ϵ_i, η_i, v_i and the M's are functions of t_i, p_i and the m's, the m's, of course, being connected by equation (2).

If we denote the mass of the i-th phase by M_i, the mass of the j-th component by $\mathfrak{M}_j$, and the energy, entropy, and volume of the whole system by E, H, V, we shall have

$$\mathrm{E} = \sum_{i=1}^{r} \mathrm{M}_i \epsilon_i, \qquad (3)$$

$$\mathrm{H} = \sum_{i=1}^{r} \mathrm{M}_i \eta_i, \qquad (4)$$

[1] Gibbs. On the Equilibrium of Heterogeneous Substances, p. 116.

$$V = \sum_{i=1}^{r} M_i v_i, \tag{5}$$

and n equations of the form

$$m_{1j}M_1 + m_{2j}M_2 + \cdots + m_{rj}M_r = \mathfrak{M}_j. \tag{6}$$

The conditions of equilibrium are found by expressing that the energy is a minimum when the entropy, volume, and masses of the independent components remain constant. That is to say, we must have

$$dE \geqq 0 \tag{7}$$

when

$$dH = 0, \quad dV = 0, \tag{8}$$

and

$$d\mathfrak{M}_j = 0, \qquad j = 1, 2, \cdots, n. \tag{9}$$

From relations (3) and (7) we obtain

$$dE = \sum_{i=1}^{r} M_i d\epsilon_i + \sum_{i=1}^{r} \epsilon_i dM_i \geqq 0,$$

or, by equation (1),

$$dE = \sum_{i=1}^{r} M_i t_i d\eta_i - \sum_{i=1}^{r} M_i p_i dv_i + \sum_{i=1}^{r} M_i \sum_{j=1}^{n} \mu_{ij}\, dm_{ij} + \sum_{i=1}^{r} \epsilon_i dM_i \geqq 0. \tag{10}$$

From equations (4), (5), and (8) we get

$$0 = \sum_{i=1}^{r} M_i d\eta_i + \sum_{i=1}^{r} \eta_i dM_i,$$

$$0 = \sum_{i=1}^{r} M_i dv_i + \sum_{i=1}^{r} v_i dM_i.$$

Multiplying the first of these equations by $-t_r$, the second by p_r, and adding the results to (10), we get

$$dE = \sum_{i=1}^{r-1} M_i (t_i - t_r) d\eta_i - \sum_{i=1}^{r-1} M_i (p_i - p_r) dv_i + \sum_{i=1}^{r} (\epsilon_i - t_r \eta_i + p_r v_i) dM_i + \sum_{i=1}^{r} M_i \sum_{j=1}^{n} \mu_{ij} dm_{ij} \geqq 0. \tag{11}$$

We have not yet taken into account equations (9), but as those

equations contain neither the η's nor the v's, and as these last quantities are capable of positive and negative variations, we obtain as conditions of equilibrium

$$t_1 = t_2 = \cdots = t_r,$$
$$p_1 = p_2 = \cdots = p_r.$$

Denoting the common temperature and pressure by t and p, relation (11) becomes

$$d\mathrm{E} = \sum_{i=1}^{r} (\epsilon_i - t\eta_i + pv_i) d\mathrm{M}_i + \sum_{i=1}^{r} \mathrm{M}_i \sum_{j=1}^{n} \mu_{ij} dm_{ij} \geqq 0. \qquad (12)$$

If we represent the mass of the j-th component which is contained in the i-th phase by M_{ij}, we shall have

$$m_{ij} = \frac{\mathrm{M}_{ij}}{\mathrm{M}_i},$$

and

$$dm_{ij} = \frac{d\mathrm{M}_{ij}}{\mathrm{M}_i} - m_{ij} \frac{d\mathrm{M}_i}{\mathrm{M}_i},$$

This relation transforms (12) into

$$d\mathrm{E} = \sum_{i=1}^{r} (\epsilon_i - t\eta_i + pv_i - \sum_{j=1}^{n} \mu_{ij} m_{ij}) d\mathrm{M}_i + \sum_{i=1}^{r} \sum_{j=1}^{n} \mu_{ij} d\mathrm{M}_{ij} \geqq 0;$$

and, finally, since

$$\mathrm{M}_{i1} + \mathrm{M}_{i2} + \cdots + \mathrm{M}_{in} = \mathrm{M}_i,$$

$$d\mathrm{E} = \sum_{i=1}^{r} (\epsilon_i - t\eta_i + pv_i - \sum_{j=1}^{n} \mu_{ij} m_{ij}) \sum_{j=1}^{n} d\mathrm{M}_{ij} + \sum_{i=1}^{r} \sum_{j=1}^{n} \mu_{ij} d\mathrm{M}_{ij} \geqq 0. \qquad (13)$$

The differentials which appear in this last relation are not all independent; we have still to take account of equations (9). If it be observed that equation (6) can be written in the form

$$\mathrm{M}_{1j} + \mathrm{M}_{2j} + \cdots + \mathrm{M}_{rj} = \mathfrak{M}_j,$$

it is seen that equations (9) impose n conditions upon the differentials $d\mathrm{M}_{ij}$. We can therefore eliminate n of these differentials from (13), and there will then remain $nr - n$ independent differentials. If they are all capable of positive and negative values (this is the case when each component occurs in each phase), we shall obtain $nr - n$ conditions by equating their coefficients to zero. These conditions will be equations between

t, p, the ϵ's, v's, μ's, and m's; or, since the ϵ's, η's, v's, and μ's are functions of t, p, and the m's, they will be equations between t, p, and the m's. The $2 + nr$ quantities, t, p, and the m's, are thus subject to r relations of the form (2), and to the $nr - n$ relations obtained from (13); there are therefore $n - r + 2$ of these quantities which are arbitrary.

If some of the differentials $d\mathrm{M}_{ij}$ are incapable of negative values (this occurs when the j-th component does not occur in the i-th phase) we cannot equate their coefficients to zero. The number of equations obtained from (13) is thus reduced; but for every equation thus lost we get an equation of the form $m_{ij} = 0$. The number of equations between t, p, and the m's is thus the same as before, and, as before, we find that $n - r + 2$ of these quantities are arbitrary.

The independent components of the system may not be independent components of each phase, that is to say, in certain phases certain of the components can enter only in definite proportions and certain other components can enter not at all. These conditions are expressed by p equations of the form

$$m_{ij} = \lambda_{ijk} m_{ik},$$

λ_{ijk} being a constant, and by q pairs of equations of the form

$$m_{ih} = 0, \quad dm_{ih} = 0.$$

As a consequence we shall have p equations of the form

$$d\mathrm{M}_{ij} = \lambda_{ijk} d\mathrm{M}_{ik},$$

and q equations of the form

$$d\mathrm{M}_{ih} = 0.$$

We now have $n + p + q$ relations between the differentials that occur in (13), and in consequence we obtain from (13) only $nr - n - p - q$ equations between t, p, and the m's. We must, however, add to these the p equations

$$m_{ij} = \lambda_{ijk} m_{ik},$$

and the q equations

$$m_{ih} = 0,$$

as well as the r relations (2). And again we find that $n - r + 2$ of the quantities in question are arbitrary.

We have thus shown that, in every case, when $n - r + 2$ of the variables, temperature, pressure, and concentrations, are chosen, the others are thereby fixed. It is worth noting also, that this choice fixes likewise the specific volumes. To complete the discussion we must examine the relations which exist between temperature, pressure, and concentrations on the one hand, and the masses of the phases, the masses of the components, and volume, on the other. The relations are given by equations (5) and (6). In the discussion of these equations it will be assumed that the $\mathfrak{M}$'s are given.

I. Suppose that $r = n + 2$. The values of the temperature, pressure, and concentrations are determinate and the system is said to be invariant. In equations (6) we can choose arbitrarily two of the masses; the remaining $r - 2$ can then be determined from the n equations, and the volume is found from equation (5). The state of an invariant system is thus absolutely fixed when, in addition to the masses of the components, the masses of two of the phases are given.

If, in addition to the masses of the components, the volume V be given, then in equations (5) and (6) we can choose the mass of only one phase arbitrarily; the remaining $r - 1$ will then be determined by the $n + 1$ equations. The state of an invariant system is thus absolutely fixed when, in addition to the masses of the components, the mass of one phase and the total volume are given.

II. Suppose that $r = n + 1$. In this case, one of the quantities, temperature, pressure, and concentrations is sufficient to determine all the others, and the system is said to be univariant. In equations (6) we can choose one of the masses arbitrarily; the remaining $r - 1$ can then be determined from the n equations, and the volume is found from equation (5). The state of a univariant system is thus absolutely fixed when, in addition to the masses of the components, the temperature and the sams of one phase, or the pressure and the mass of one phase, are given.

If, in addition to the masses of the components, the volume of the system be given, the $n + 1$ equations (5) and (6) will determine the masses of the phases. The state of a univariant system is thus absolutely fixed when, in addition to the masses of the components, the temperature and the volume, or the pressure and the volume, are given.

III. Suppose that $r = n$. In this case, two of the quantities, temperature, pressure and concentrations determine the others, and the system is said to be divariant. If the temperature and the pressure be given, the concentrations are thereby fixed and equations (6) and (5) give the masses of the phases and the volume. The state of a divariant system is thus absolutely fixed when, in addition to the masses of the components, the temperature and the pressure are given.

Suppose that the temperature and the volume are given. The condition that equation (5) should be compatible with equations (6) is expressed by an equation between the concentrations and the specific volumes. As all these quantities are functions of the temperature and the pressure, and as the temperature is given, this equation determines the pressure. Similarly, when the pressure and the volume are given the temperature will be fixed. The state of a divariant system is thus absolutely fixed when, in addition to the masses of the components, the temperature and the volume, or the pressure and the volume are given.

A special case worth noticing occurs when equations (6) do not determine the masses, that is when

$$\begin{vmatrix} m_{11} & m_{21} & \cdots & m_{r1} \\ m_{12} & m_{22} & \cdots & m_{r2} \\ \vdots & \vdots & & \vdots \\ m_{1r} & m_{2r} & \cdots & m_{rr} \end{vmatrix} = 0.$$

But as the concentrations are all functions of the temperature and the pressure, this is really an equation between the temperasure and the pressure. The temperature, then, will determine the pressure and the concentrations. Completely to define the

state of the system, we must in addition choose the mass of one of the phases or the volume.

IV. Suppose that $r < n$. The system is said to be polyvariant, for after choosing the temperature and the pressure we shall still have to fix $n - r$ of the concentrations before the others are determined. Now, the conditions that the n equations (6) should be compatible are expressed by $n - r$ equations between the concentrations. Choosing the $n - r$ independent concentrations so that these conditions are satisfied, the masses of the phases and the volume are determined. The state of a polyvariant system is thus absolutely fixed when, in addition to the masses of the components, the temperature and the pressure are given.

Suppose that the temperature and the volume are given; the pressure and $n - r$ of the concentrations are still arbitrary. But the conditions that equations (5) and (6) should be compatible are expressed by $n - r + 1$ equations between the concentrations and the specific volumes. Choosing the pressure and the $n - r$ independent concentrations so that these equations are satisfied, the state of the system is determined. Similarly, when the pressure and the volume are given the temperature and the $n - r$ independent concentrations will be fixed. The state of a polyvariant system is thus absolutely fixed when, in addition to the masses of the components, the temperature and the volume, or the pressure and the volume, are given.

It may be noted, finally, that in each case the state of the system is determined by the masses of the components and two additional variables. In the case of divariant and polyvariant systems we may choose as the additional variables any two of the three quantities, temperature, pressure, and volume. For univariant systems we may take as variables the temperature and the volume, or the pressure and the volume, but not the temperature and the pressure.

Université de Bordeaux, January, 1899.

THE EQUILIBRIA OF STEREOISOMERS, III

BY WILDER D. BANCROFT

This paper is devoted to the discussion of the changes of equilibrium when a substance that exists in two modifications in the melt is brought in contact with another component which can form a solid compound with one or both of the modifications. Passive resistances to change are excluded explicitly. As in the previous papers[1] the modification that has a stable melting-point will be called the α modification, while the form having no stable melting-point will be known as the β modification. The other component will be called the component C. If the component C forms a compound both with the α and the β modification we may consider four possibilities.

I. The α modification, the α compound and the component C can each exist in stable equilibrium with solution and vapor.

II. The α modification, the β compound and the component C can each exist in stable equilibrium with solution and vapor.

III. The α modification, the α compound, the β compound and the component C can each exist in stable equilibrium with solution and vapor.

IV. The α modification, the β modification, the β compound and the component C can each exist in stable equilibrium with solution and vapor.

The diagram for Case I is given in Fig. 1.[2] The melting-point of the α compound is denoted by H and that of the β compound by K; the dotted line HK represents the freezing-point curve for mixtures of the two compounds. Since a system of the type under discussion behaves like a three-component sys-

[1] Jour. Phys. Chem. **2**, 143, 245 (1898).

[2] The letter S has been omitted in the diagram from the intersection of RC with EI.

tem provided we work rapidly, it will therefore be possible to realize the boundary curves LV, EI, FI, IV, VO, GO and DO. The solid phases are the *a* modification and the *a* compound along LV, the *a* compound and the component C along EI, the component C and the *β* compound along FI, the *a* compound and the *β* compound along IV, the *a* modification and the *β* compound along VO, the *β* compound and the *β* modification along GO, the *β* and the *a* modifications along DO. The arrowheads point in the direction of rising temperature as deduced by

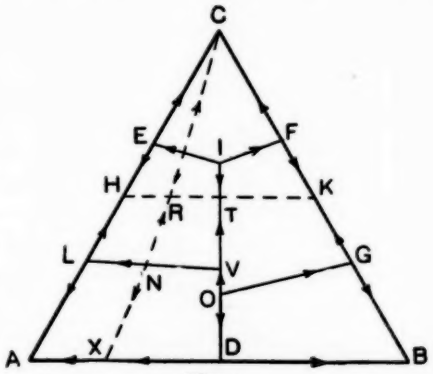


Fig. 1

applying the theorem of van Rijn van Alkemade. For the purposes of discussing this particular case, it is immaterial whether the point O or the point V lies nearer the point D. If the relative positions of the two points were reversed, the only difference would be that the *a* compound and the *β* modification would be the solid phases along VO instead of the *β* modification and the *a* compound as now. The boundary curve for the two modifications would of course then be DV instead of DO.

If we work very slowly so that equilibrium will be reached, the boundary curves will be represented by the dotted line XNRSC. Here X is the stable triple point with the *a* modification as solid phase; N is the stable quadruple point with the *a* modification and the *a* compound as solid phases; S is the

stable quadruple point with the *α* compound and the component C as solid phases. The *α* modification is solid phase along XN, the *α* compound along NRS and the component C along SC. Since the curve for stable equilibrium XNRSC does not cut the fields for the *β* modification or the *β* compound, neither of these substances can exist in stable equilibrium with solution and vapor. Along the curve XNRSC the temperature rises from N to X and to R, and from S to R and to C. The equilibrium curve cuts HTK at R and this is therefore the highest temperature at which the *α* compound can exist in stable equilibrium with solution and vapor. If there is any satisfactory way of determining analytically the amount of either of the modifications in the melt, the actual determination of the stable and the instable boundary curves will present no difficulty provided the reaction velocity be not too great. In the majority of cases rapid quantitative separations will be impossible and it will therefore be worth while to consider how approximate results can be obtained without making any analyses. It is clear that the greater the reaction velocity, the more fleeting will be the composition of an instable phase and therefore the greater the experimental error. In order to avoid unnecessary complications we will assume that the rate of change is very small. The concentration of the solution about AXDB can be determined by mixing the *α* and *β* modifications in varying proportions and determining the melting-points and freezing-points of the mixtures, as has been done by Cameron[1] with the two benzaldoximes. Owing to the fairly rapid heating that is essential, this method is anything but accurate. No one would dream of determining the solubility of a salt in water in this way. If, however, one cools the melt as soon as the last solid particle has disappeared and if one determines the temperature at which the solution begins to freeze, one has a check on the results. Barring a displacement of the equilibrium, the temperature of final liquefaction would be the same as the temperature of initial solidification in case there were no experimental error. When

[1] Jour. Phys. Chem. **2**, 409 (1898).

the two differ — as they always will — the true temperature lies between the two observed. When the mixture has the composition denoted by the point X the error due to a displacement of equilibrium at constant temperature becomes zero and therefore this point can be determined with a certain degree of accuracy. The curve HRTK can be determined in a similar way by taking mixtures of the two compounds. In an analogous manner it will be possible to determine ALHEC and BGKFC. If a quantitative study of the whole system be desired, there seems to be no other way than to make a series of ternary mixtures and determine the fusion points. The error here would of course be greater than with the binary mixtures. This would also involve a larger amount of material than will usually be available. For most purposes a qualitative determination of XNRSC will be all that is necessary. This can easily be made. The temperatures of X and R can be found readily and there is no difficulty in telling which form is the more stable. We can next start at X and add varying amounts of C determining the freezing-points at equilibrium. This will give us the temperatures and the amounts of C corresponding to the stable boundary curve XNRSC. If there are only two quadruple points, N and S, and the α compound is the stable one, the system must belong under Case I. It is clear that if quantitative determinations of X and R be made, a very good guess can be made as to the rest of the curve, and it would be a simple matter, if desired, to verify a couple more points on the curve.

The diagram for Case II is given in Fig. 2. The letters have the same significance as in the preceding diagram[1] except that S is now the stable quadruple point with the β compound and the component C as solid phases. The point N has disappeared and the point M represents a stable quadruple point with the α modification and the β compound as solid phases. The equilibrium curve is XMRSC. An inspection of the diagram shows that the addition of the component C displaces the

[1] To avoid crowding there is no arrowhead on OV. The temperature rises from O to V and to D.

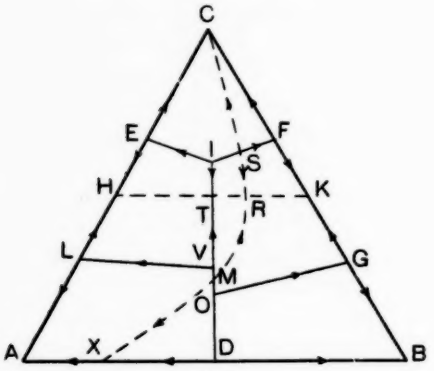


Fig. 2

equilibrium between the two modifications to such an extent that the curve for stable equilibrium no longer cuts the boundary curve LV, cutting VO instead. The β compound will therefore be the stable form and not the α compound. This system can be recognized as easily as the preceding one. If there are only two

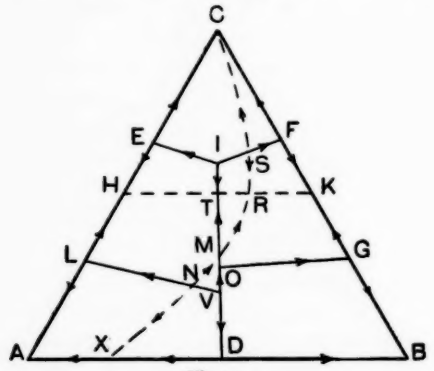


Fig. 3

quadruple points on the curve XMRSC and the β compound is stable, the system comes under Case II.

The diagram for Case III is given in Fig. 3. The instable boundary curves are the same as in the two preceding diagrams

except that the point V lies between the points D and O. The stable boundary curve is represented by XNMRSC. The displacement of equilibrium by addition of the component C is not so marked as in the preceding case and the curve for stable equilibrium enters the field for the α compound at N and the field for the β compound at M. The point N is a stable quadruple point with the α modification and the α compound as solid phases; the point M is a stable quadruple point with the α and the β compounds as solid phases while S is the third quadruple point with the β compound and the component C as solid phases. Both the α and the β compounds can thus be in stable equilibrium with solution and vapor; but the β compound would ordinarily be called the 'stable' form because it is the form that is stable when one starts with either of the pure compounds. The temperature rises along the equilibrium curve from S to R and to C, from N to R and to X, the temperature of the point M being necessarily higher than that of the point N because a solution containing less of the component C than the compounds cannot solidify to a mixture of the two compounds. This case can be distinguished from the preceding two by there being three quadruple points. While it is possible theoretically to detect the existence of a third quadruple point by plotting the observed freezing-points against the percentage composition C and determining the sudden changes of direction, it will always be safer to check this result by studying the rate of cooling of each mixture, plotting freezing-points against time. This case can be distinguished from Case IV by the temperature of the second quadruple point M, being higher than that of the first quadruple point N.

The diagram for Case IV is given in Fig. 4. The instable boundary curves are the same as in the preceding case. The stable boundary curve is represented by the curve XQMRSC, where Q is a stable quadruple point with the α and β modifications as solid phases. The other letters have their usual significance. The temperature rises along the equilibrium curve from S to C and to R and from M to X and to R. The temperature

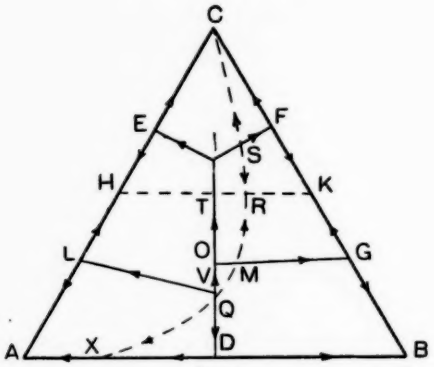


Fig. 4

of the point Q must be higher than that of the point M because a solution containing the component C cannot solidify to a mixture of two phases neither of which contain C. This case can be distinguished from Cases I and II by there being three stable quadruple points instead of two; it can be distinguished from Case III by the temperature of the second quadruple point being lower than that of the first. The four cases are thus easily distinguishable. Since the stable quadruple point S is common to all four cases we may ignore it and formulate our general rule as follows: To identify a system take different mixtures of the stable modification and the stable compound and determine the number and temperatures of the stable quadruple points.

1. If the *α* compound is the stable one and but one stable quadruple point is found the system comes under Case I.

2. If the *β* compound is the stable one and but one stable quadruple point is found the system comes under case II.

3. If the *β* compound is the stable one and two stable quadruple points are found, the system comes under Case III, provided the quadruple point nearer the stable triple point has the lower temperature.

4. If the *β* compound is the stable one and two stable quadruple points are found, the system comes under Case IV, provided the quadruple point nearer the stable triple point has the higher temperature.

While these four are without doubt the most important cases, there is at least one other that is possible on paper. In Fig. 3 the curve for stable equilibrium could have been drawn so that the point M lay between T and I instead of between T and V. The point R would then lie in the field for the *a* compound which would thus become the 'stable' compound. Such a system presents no difficulties from a graphical point of view; but somehow it seems improbable chemically. There would be no difficulty in recognizing such a system if it did occur, because there would be two stable quadruple points between R and C. Of course, everyone understands that the curves IV, VO and OD do not form a straight line and that there will be a change of direction at each quadruple point. There seemed to be no object in representing this in the diagrams where the aim was to reduce everything to first principles and to present only the essential skeleton.

There is one point however that calls for special mention. The quantitative determination of the instable boundary curves by observing the fusion points of mixtures is an unsatisfactory method at best. It becomes a hopeless one in case the compound behaves, for instance, like phthalic acid, dissociating into phthalic anhydrid and water.[1] Under these circumstances there would be, theoretically, two instable concentration-temperature surfaces; one when the compound has neither dissociated nor changed over and the other when the compound has dissociated, but has not yet changed over. That such a state of things is not impossible is shown by the fact that with fumaric and maleic acids we have the fumaric acid changing below its melting-point[2] into maleic anhydrid and water. This differs from the case we have been discussing in that there is only one anhydrid and not two. This possibility of dissociation, though playing havoc with quantitative determinations of the instable boundary curves, does not affect the qualitative determination of the curve of

[1] Jour. Phys. Chem. **3**, 72 (1899).

[2] Although maleic acid in water certainly changes into fumaric acid above 100°, it seems not improbable that at ordinary temperatures we may have a case of passive resistance. See Skraup. Monatsheft. **12**, 107 (1891).

stable equilibrium. On the other hand, if the instable compound has not been isolated, its existence can be predicted from the fact of the stable compound having a variable freezing-point only in case it is shown that this variation is not due to dissociation.

So far it has been assumed explicitly that the component C forms a compound with both the modifications. This is not necessarily the case and it will therefore be desirable to consider at least one system in which only one compound is formed. The diagram marked Fig. 5 illustrates a case in which the β

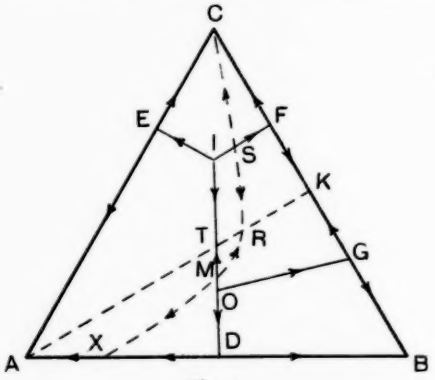


Fig. 5

compound is possible and is stable while the α compound does not exist. The further assumption involved is that any change due to dissociation of the compound at melting is so rapid that it cannot be detected without special effort.

The lettering of the preceding diagrams has been kept as far as possible. The line HK has disappeared with the field for the α compound and has been prepared by the line ATRK connecting the melting-points of the α modification and the β compound. The curve for stable equilibrium is represented by XMRPSC. One would naturally expect R to be the highest stable melting-point at which the β compound can be in equilibrium with solution and vapor; but this view presents a serious difficulty. A

maximum melting-point should mean a constant melting-point. A solution having the composition of the point R cannot solidify without change of temperature because the solution has not the composition of the solid phase, the β compound. We are therefore forced to the conclusion that the maximum temperature along MRS is not at R but at P, the point (omitted from the diagram by mistake) at which a line through K parallel to BA cuts RS. If it could be shown that a maximum freezing-point was not necessarily a constant freezing-point then the temperature of the point R might be higher than that of the point P. This, however, seems improbable,[1] though the converse proposition that a constant melting-point is not necessarily a maximum or a minimum is known to be true for some systems forming solid solutions. If the point P is a maximum temperature the point M may lie on the other side of T.

Of course, there are other cases conceivable, in which the α compound is the only one and is stable; in which the β compound is the only one and is not stable; in which the β modification is the stable, etc., etc. Since these cases do not, at present, appear to offer any points of especial interest, this brief reference to them will suffice and we can now consider some of the experimental data referring to the different cases that have been discussed.

In the hydrochlorids of the aromatic aldoximes some of the conditions required by the theory are realized. Benzaldoxime occurs in two modifications, the α form melting at 35° and the β form melting at 132°, the former being the more stable. Two hydrochlorids are known, the α compound melting at 105° and the β compound melting at 67°. Of these the β compound is the more stable.[2] We have thus a reversal of stability. It appears improbable that this system should belong under Case IV. The experimental data are not sufficient to enable us to decide between Cases II and III. It is stated that the α hydrochlorid crystallizes as stable form from cold ether. If this is

[1] Cf. Miller, Jour. Phys. Chem. **1**, 505, (1897).

[2] Meyer and Jacobsen. Lehrbuch, **2**, 511.

correct there must be an inversion temperature for the two hydrochlorids and this may lie above the temperature of the point O. If this is not so, this system will come under Case II. Trimethyl benzaldoxime occurs in two modifications and two hydrochlorids have been isolated, of which the β compound is the more stable.[1] I have not been able to find any record of addition compounds of the aldoximes where the α compound is the more stable. On the other hand, the sodium salt of the α-benzaldoxime is more stable than the sodium salt of the β-benzaldoxime. If the ammonium salts of the two benzaldoximes could be prepared we should have a system coming under Case I. The system fumaric acid, maleic acid and ammonia comes under Case I, as do also all systems composed of ammonia and two mutually convertible acids.

With anisaldoxime only the β-hydrochlorid has been isolated. There is nothing to show whether the α-hydrochlorid can exist or not. If it cannot exist, this system would then be represented by the diagram in Fig. 5. Chloral and water would appear to be a case of this kind provided we assume that metachloral is the stable form. Unfortunately, we do not really know enough about the reversible transformations of chloral and metachloral to enable us to speak definitely.

Since the form of the equilibrium curve is the most important feature in determining the equilibrium phenomena, it is necessary to consider what predictions can be made with regard to the displacement of equilibrium on adding a component C, irrespective of whether C does or does not form a compound with one or both of the modifications. Anything that changes the chemical potential of either of the reacting substance wills displace the equilibrium. It has been shown by Miller[2] that, for a given concentration, the chemical potential of the solute is lower, the more soluble the solute is in the solvent. In other words adding a component C will displace the equilibrium in

[1] Hantzsch and Lucas. Ber. chem. Ges., Berlin, **28,** 744 (1895); Lucas. Ibid. **29,** 956 (1896).

[2] Jour. Phys. Chem. **1,** 636 (1897).

such a way as to increase the concentration of the more soluble modification. There are as yet no data to establish this point for stereoisomers where the component C forms compounds neither with the *a* nor with the *β* modification; but fortunately the aldoximes illustrate the point when we treat with acid or alkali. It is clear that if one of the modifications is more alkaline than the other it will be the more stable in the presence of acids, while the reverse will be true in alkaline solutions. It has been pointed out that the hydrochlorid of *β*-aldoxime is the more stable and the sodium salt of the *a*-benzaldoxime. The two sodium salts have been prepared and studied by Goldschmidt Röder.[1] It was found that the sodium salt of the *a* modification was dissociated electrolytically in aqueous solution, while the sodium salt of the *β* modification underwent hydrolysis, the solution containing free oxime and alkali. This result was interpreted correctly by Goldschmidt and Röder without reference to the chemical potential. Stress has been laid upon it here to bring out the relation between this phenomenon and the effect due to adding benzene or any other so-called indifferent solvent.

In this paper there has been given a fairly complete classification of the equilibria to be expected when two mutually convertible modifications are brought in contact with a substance capable of forming compounds with one or both of the modifications. It has been shown that Duhem's theory enables us to predict reversals of stability, instances of which are known experimentally. The conditions under which displacement of equilibria occur have also been outlined.

Cornell University

[1] Ber chem. Ges. Berlin, **28**, 2013 (1895).

ON THE MOLECULAR WEIGHT OF SULPHUR IN CARBON DISULPHIDE SOLUTIONS

BY H. T. BARNES

Orndorff and Terrasse have shown[1] in a very extensive series of determinations of the molecular weight of sulphur that in solutions of metaxylene, phenetol, phenol and naphthalene the molecular complex at the boiling-point is represented by 256 or S_8. Their results in solutions of carbon disulphide, benzene and toluene show 288 or S_9. Their freezing-point determinations point to S_8 and even to S_7.

Aronstein and Meihuizen[2] find on the contrary that in CS_2 sulphur has the value S_8. It becomes a matter of interest to study this point further and to see what can be learned from a consideration of the density of solutions of S in CS_2.

It has been shown[3] that for salt solutions the amount of water displaced by the salt bears a fairly approximate molecular relation to the amount of salt added. This molecular ratio may be represented by even numbers of molecules of water to one molecule of the salt, and for the salts investigated the ratio was either 1, 2, or 3. It appears then that what may be called the effective volume occupied by the molecules of different salts in solution differ, but that this varies by whole numbers. No attempt was made to discuss this question in the paper above cited or the effect of dissociation on the effective sizes of the salt molecules, for it is unlikely that the total space occupied by a salt molecule dissociated or undissociated would differ very much, it would likely depend on the interspacial relations. Hence what relation does the molecule

[1] Am. Chem. Jour. **18**, 173 (1896).

[2] Chem. Centralblatt, **2**, 1194 (1898).

[3] Barnes and Scott. Jour. Phys. Chem. **2**, 536 (1898).

of sulphur have in solution to the number of molecules of CS_2 it displaces? We are met with a difficulty at the outset in the question as to the effective volumes of the CS_2 and S molecules. Can it be said that the molecules have the same effective size or different, if different, then in all probability they will differ by a whole number as in the case of the salt molecules. So although the absolute value of the S molecule may not be obtained by a study of the density of sulphur solutions, yet it will be possible to say whether sulphur may be represented by S_8 or S_9. Accepting the lowest limit 76 for the molecular weight of CS_2 then the weight of sulphur should be some multiple either of S_8 or S_9.

The most trustworthy determinations of the density of sulphur solutions in carbon disulphide are those of Pfeiffer.[1] He has given the following direct measurements in Table I.

TABLE I

% S	Spez. Gew.	% S	Spez. Gew.
0	1.2708	12	1.3297
2	1.2802	14	1.3399
4	1.2901	16	1.3502
6	1.2998	18	1.3604
8	1 3096	20	1.3709
10	1.3195		

The density is expressed in terms of water at 4° C. Taking the density d and multiplying by the percent weight p and dividing by 100, the weight w of S in 1 cc of solution is obtained. Adding to this the weight of 1 cc of CS_2 a theoretical density is obtained, assuming there be no change in volume on the addition of sulphur. The amount of CS_2 displaced by the sulphur is given by differencing the calculated and observed densities. In Table II are given the numbers deduced from Pfeiffer's observations.

[1] Zeit. anorg. Chem. **15,** 194 (1897). The author desires to express his thanks to Prof. Bancroft for having these determinations copied off and sent to him.

TABLE II

p	d	w	$1.2708 + w$	$-d$	$\frac{76}{128}w$
0	1.2708	0	0	0	0
2	1.2802	0.0256	1.2964	0.0162	0.0152
4	1.2901	0.0516	1.3224	0.0323	0.0307
6	1.2998	0.0780	1.3488	0.0490	0.0463
8	1.3096	0.1048	1.3756	0.0660	0.0622
10	1.3195	0.1320	1.4028	0.0833	0.0784
12	1.3297	0.1596	1.4304	0.1007	0.0948
14	1.3399	0.1876	1.4584	0.1185	0.1114
16	1.3502	0.2160	1.4868	0.1366	0.1283
18	1.3604	0.2449	1.5157	0.1553	0.1454
20	1.3709	0.2742	1.5450	0.1741	0.1628

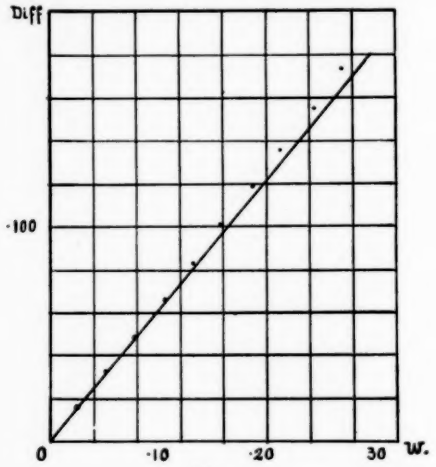


Fig. 1

The plot of w and $(1.2708 + w) - d$ shows very clearly the regularity of the observations. On the same plot the last column of the table is represented by a straight line which gives the relation

$$\frac{76}{128}w, \text{ or } \frac{CS_2}{S_4}w,$$

as representing the weight of displaced CS_2. The line falls below the observed density line but is very much closer than any other relation. The agreement is fair considering the difficulty of avoiding error in determining the densities of CS_2 solutions. It appears then that these results point to a molecular weight for sulphur of S_8 instead of S_9. Whether it should be S_4 depends of course on the relative effective sizes of the molecules.

McGill University, Feb. 21, 1899

FREEZING-POINT IN TERNARY MIXTURES

BY JOHN WADDELL

McIntosh states as the result of his work[1] that the addition of a substance to a binary solution in equilibrium with a solid phase, raises the freezing-point if the substance added be nonmiscible with the component appearing as the solid phase. On the other hand the freezing-point is lowered if the component added be nonmiscible with the component which does not appear as solid phase and the lowering is greater than if the substance were added to the pure solvent. In the third case, where the three components are miscible, the sum of the single depression is usually greater than the depression for the mixture.

A peculiar modification of the last case is when the solutes are readily miscible with each other and one solute readily miscible with the solvent while the second solute is but sparingly miscible with the solvent at the temperature of the experiments. If the components of a binary solution be A and B, of which A is the one separating in the solid phase, the addition of a third substance C slightly miscible with A and readily miscible with B might be expected to lower the freezing-point till a certain quantity of it was added and then to cause a rise in the temperature of freezing. I have made some experiments with a view to obtaining this result and though I have not hit upon a combination of substances which is ideal, I have arrived at some results which indicate that the general conception of the case is correct.

Water was chosen as the solvent which was to separate in the solid phase. The readily soluble solute chosen was acetone, and a number of substances sparingly soluble in water and readily soluble in acetone were experimented with.

[1] Jour. Phys. Chem. 1, 492 (1897).

Table I gives a series of determinations of the lowering of the freezing-point of water by the addition of acetone alone. The first column gives the number of grams of acetone in one hundred grams of water; the second column gives the corresponding lowering of the freezing-point; while the third column gives the molecular weight of acetone as calculated by the formula $M = \frac{g}{\Delta} \times 18.5$. Those determinations were not all

TABLE I

g	Δ	$\frac{g}{\Delta} \times 18.5$	g	Δ	$\frac{g}{\Delta} \times 18.5$
0.483	0.16	55.9	11.40	3.43	61.5
1.42	0.46	57.0	11.83	3.65	60.0
1.72	0.56	56.8	12.45	3.82	60.1
3.08	0.96	59.4	13.62	4.25	59.3
3.99	1.22	60.5	14.20	4.50	58.3
4.11	1.29	58.9	14.76	4.44	61.5
4.38	1.38	58.5	17.50	5.34	60.6
6.78	2.13	58.9	21.18	6.35	61.6
7.31	2.21	61.2	23.12	7.11	60.1
8.63	2.67	59.7	24.84	7.62	60.2
10.21	3.11	59.7	27.00	8.41	59.3
10.38	3.09	62.1	27.61	8.34	61.3
11.40	3.44	61.2			

made in one series; a number of them were obtained when determining the freezing-point of a mixture of water and acetone preparatory to adding the second solute.

Salicylic acid was first experimented with. It was found to be more sparingly soluble in water at 0° C. than was expected from the solubility given in the books for higher temperatures; 100 grams of water dissolve 0.187 gram of salicylic acid. The freezing-point of the water was lowered by an amount between 0.02° C. and 0.025° C., which corresponds to the normal depression for the undissociated molecule. A depression of 0.023° C. gives a calculated molecular weight 146, while that of salicylic acid is 158. When acetone was present with the water, I did not in any case get a depression of the freezing-point, but on the other hand I did obtain *one* mixture in which there was no rise. Table II gives the numbers obtained. In this and in all the other

TABLE II

Acetone	Salicylic acid	Δ
3.08 g	0.190 g	±0.00°
10.21	0.283	+0.02
27.61	0.046	+0.01
27.61	0.177	+0.18

tables the quantities of the solute are expressed in grams per hundred grams of water. The first and last lines of Table II show the difference depending upon the relative quantity of acetone. When there was a small proportion of acetone, the lowering of the freezing-point of the water by the solution of the salicylic acid in it, was just neutralized by the withdrawal of the acetone, which tends to raise the freezing-point.

Tables III and IV show that phenol and paranitrophenol are very similar in their action to salicylic acid.

TABLE III

Acetone	Phenol	Δ
23.12 g	1.262 g	+0.12°
	1.754	+0.21
	2.344	+0.35
	saturated	+0.46

TABLE IV

Acetone	Paranitrophenol	Δ
14.76 g	0.066 g	+0.005°
	0.133	0.025
	0.250	0.035
	0.330	0.065
	0.430	0.095
	0.530	0.12
	0.643	0.14

In Table V the results are given with hydroquinone, and

TABLE V

Acetone	Hydroquinone	Δ
9.71 g	0.755 g	±0.00°
	1.184	+0.05
	2.667	0.07
	3.08	0.09
	4.09	0.14
	5.46	0.19

since 0.754 g of hydroquinone gives neither risen or depression of freezing-point it would seem that with a smaller amount of hydroquinone than that, a *lowering* of the freezing-point might be noticed. The normal lowering of the freezing-point by 0.755 gram of hydroquinone in a simple aqueous solution is 0.127° C. Salicylic acid, phenol, paranitrophenol and hydroquinone all seemed too little soluble in water to permit of detecting readily a lowering of the freezing-point of water when they were added to the water containing acetone. It was hoped that ether might show the lowering of freezing-point to a minimum, and that afterwards there might be a rise. The results were not so satisfactory as could be wished. In the cases examined the freezing-point was lowered down to the point where two liquid layers appeared.

Table VI gives the depression obtained on the addition of

TABLE VI

Acetone	Ether	Δ	Δ
9.83 g	2.77 g	−0.44°	−0.69°
	4.90	1.13	−1.22
	6.55	1.48	1.64

comparatively small quantities of ether. Δ is the depression of freezing-point in the acetone and water, Δ_1 is the calculated depression for ether in water alone. Δ is less than Δ_1.

In Table VII there is a continuation of the same experi-

TABLE VII

Acetone	Ether	Δ
9.83 g	17.91 g	−0°
	20.66	−0.25
	23.45	0.70
	large excess (two layers)	0.35

ment, but as I had passed the limits of the reading of the thermometer it needed to be reset, and the temperature reading when there were 9.83 grams of acetone and 17.91 grams of ether was called zero. When there was a large excess of ether the freezing-point of the lower layer was raised, but that may well

be due to the lower aqueous layer containing less acetone than was contained in the one liquid phase.

Table VIII exhibits much the same condition with a larger

TABLE VIII

Acetone	Ether	Δ	Δ_1
27.0 g	1.597 g	—0.29°	—0.40°
	3.63	0.52	0.89
	7.83	more than —1.00	

quantity of acetone in solution. Δ is in this case also, less than Δ_1 which is to be expected. The readings went below the limit of the thermometer, which accounts for the last reading of the table being given in the form there shown. With such comparatively large quantities of acetone and ether, the freezing-point was so near the temperature of the freezing mixture that experimenting became tedious.

NEW BOOKS

Die Continuität des gasförmigen und flüssigen Zustandes. *Theil I. By J. D. van der Waals. Second, revised, edition. 15 × 23 cm; pp. iv and 182. Leipzig: Johann Ambrosius Barth, 1899.* — In the present volume, van der Waals has reprinted the German edition of his famous dissertation on the continuity of the aeriform and liquid states. He has appended a few notes with the purpose of adding clearness to the text as it originally stood. These additions are confined to a reviewing comment upon the chapters on the influence of the composition and extension of the molecules; to a study of the course followed by the difference of the two specific heats when the density is varied; and to an examination, at the close, of the form of the function *b*.

The promised second part of the work is to present van der Waals's theory of capillarity, and the form that his theory assumes for fluid mixtures of two components. The whole is planned to be a digest of his own researches, and not at all a general account of all the investigations that have been pursued in this field. It has, of course, great interest, as affording an introduction of the author's remarkable theory. The volume is gotten up in the publisher's usual attractive style. *J. E. Trevor*

Vorlesungen über Gastheorie. *By Ludwig Boltzmann. II. Theil: Theorie van der Waals'; Gase mit zusammengesetzten Molekülen; Gasdissociation; Schlussbemerkung. 14 × 22 cm; pp. x and 265. Leipzig: Johann Ambrosius Barth, 1898.* — In the preface to this, the second, volume of Boltzmann's treatise on the kinetic theory of gases, Boltzmann says:

"When the first Part of my Theory of Gases was printed, I had almost entirely ready a manuscript for the present second and concluding part, in which the more difficult portions of the theory were not considered. But, just at that time, renewed attacks were made upon the theory of gases. Now I am convinced that these attacks are due solely to misconceptions, and that the rôle of the theory in science is by far not closed. The abundance of the results which van der Waals has deduced from the theory and which are in accord with the facts, I will endeavor to make apparent in the book. More recently, too, the theory has again afforded indications that could have been obtained in no other way. From the theory of the ratio of the specific heats Ramsay has determined the atomic weight of argon, and consequently the position of this element in the periodic system; which position later, through the discovery of neon, he has proved to be correct. And in like wise Smoluchowski has deduced from the kinetic theory of the conduction of heat the existence and the magnitude of the temperature-drop in the conduction of heat in very dilute gases.

"It would, therefore, in my opinion, be a loss to science, if the theory of gases were temporarily to fall into neglect because of the opposition that rules at present; as happened, for example, in the case of the undulation theory, through the authority of Newton.

"I am aware how impotent the individual is as opposed to the tendencies of the age. But, nevertheless, in order to do all in my power to prevent that too much should have to be rediscovered when return is made to the theory of gases, I have included in the present

book the more difficult parts of the theory, those parts that are most subject to misapprehension; and I have endeavored to give the most intelligible presentation possible of at least their outlines. In consequence of these I must, indeed, beg for indulgence if some of the chapters have thereby become rather long; for a reasonably precise presentation of the theories in question is hardly possible without employment of the corresponding mathematical apparatus."

The seven chapters of the book are entitled, respectively: Outlines of the theory of van der Waals; Physical discussion of the theory of van der Waals; Theorems of general mechanics that are useful in the theory of gases; Gases with compound molecules; Deduction of van der Waals's equation by means of the idea of the virial; Theory of dissociation; Additions to the theorems relative to thermal equilibrium in gases with compound molecules. The lucidity and splendid style of the author are too well known to need comment here. And, notwithstanding his disclaimer, the compass of the present volume is very moderate — but 265 small pages. Those who are really interested in the kinetic theory of gases should be thankful for the appearance of the book.

J. E. Trevor

Einführung in die mathematische Behandlung der Naturwissenschaften. *By W. Nernst and A. Schönflies. Second Edition; 17 × 25 cm; pp. xii and 339. München: E. Wolff, 1898. Price: bound, 10.50 marks.* —The useful little compendium, by Nernst and Schönflies, of the mathematics that oftenest find employment in the physical sciences, and more especially in physical chemistry, has now reached a second edition, but three years after its first appearance in 1895. In the revision, the plan of the book has not been altered, and but little material has been added. The topics considered are, successively, analytical geometry, differential and integral calculus, and the solution of algebraic equations; to which are appended a lot of illustrative practical examples, a reference collection of formulas, and a very satisfactory exposition, in twelve pages of the subject of determinants. The only serious defect noted by the reviewer is the absence of any treatment of Fourier's series.

J. E. Trevor

Ostwald's Klassiker der exacten Wissenschaften. *12 × 19 cm. Leipzig: W. Engelmann, 1898.*

No. 93. Drei Abhandlungen über Kartenprojection. By Leonhard Euler (1777). Edited by A. Wagnerin. 77 pp. 1.20 marks.

No. 94. Ueber das' Verhältniss zwischen der chemischen Zusammensetzung und der Krystallform arseniksaurer und phosphorsaurer Salze. By Eilhard Mitscherlich (1821). Edited by P. Groth. 59 pp. 1.00 mark.

No. 95. Pflanzenphysiologische Abhandlungen. By Ernst von Brücke (1844-1862). Edited by S. Fischer. 86 pp. 1.40 marks.

No. 96. Optik; oder Abhandlung über Spiegelungen, Brechungen, Beugungen und Farben des Lichts. I. Buch. By Isaac Newton (1704). Edited by William Abendroth. 132 pp. 2.40 marks.

No. 97. Optik; oder Abhandlung über Spiegelungen, Brechungen,

Beugungen und Farben des Lichts. II. und III. Buch. By Isaac Newton (1704). Edited by William Abendroth. 156 pp. 2.40 marks.

No. 99. Ueber die Bewegende Kraft der Wärme, und die Gesetze welche sich daraus für die Wärmelehre selbst ableiten lassen. By. R. Clausius (1850). Edited by Max Planck. 55 pp. 0.80 marks.

No. 101. Abhandlungen über Mechanische Wärmetheorie. By G. Kirchhoff (1858). Edited by Max Planck. 48 pp. 0.75 marks.

No. 102. Ueber Physikalische Kraftlinien. By James Clerk Maxwell. Edited by L. Boltzmann. 146 pp. 2.40 marks.

We have to announce the appearance of a number of new volumes of Ostwald's admirable little *Klassiker* series. The reprint of Euler's three papers supplements the previously published volumes on the mathematical theory of map construction. Mitscherlich's famous paper is accompanied by an interesting account of the author's life and scientific career. The volume of researches in plant physiology comprises four papers by Brücke. Newton's great 'Optiks' is presented in two carefully annotated volumes, to the first of which is attached a portrait of Newton. Numbers 99 and 101 of the series present in handy form two of the great thermodynamic classics: Clausius's paper of 1850 on the general theory of reversible thermodynamics, and Kirchhoff's (three) papers of 1858 on the representation of the energy of a body by integrals, on the heat of dilution, the intersection of sublimation and vaporization curves, the absorption of gases by liquids, and the temperature coefficients of energy differences. Both are edited by Planck, aud both should be in the hands — and in the minds — of everyone who cares for the theory of physical chemistry. The last volume in the list is a richly and most delightfully annotated edition, by Boltzmann, of a series of Maxwell's papers on electromagnetism.

J. E. Trevor

Die Fortschritte der Physik. *Dargestellt von der physikalischen Gesellschaft zu Berlin. Im Jahre 1896: III. Abtheilung: Kosmische Physik; redigirt von Richard Assmann; pp. xliv and 531. Im Jahre 1897; I. Abtheilung: Physik der Materie; redigirt von Richard Börnstein; pp. lxxii and 573. II. Abtheilung: Physik des Aethers; redigirt von Richard Börnstein; pp. lii and 912. III. Abtheilung: Kosmische Physik; redigirt von Richard Assman; pp. xliv and 566. 16 × 23 cm. Braunschweig: F. Vieweg und Sohn, 1898.* — Four more parts of the *Fortschritte der Physik* have recently appeared, concluding the report of progress for the year 1896, and completing that for 1897. The comprehensive scope and careful editing of the work continue to be all that they have been in the past; and, as is natural, the reports of physicochemical work are, as before, extended and complete. The value of this series of carefully written abstracts, in giving a summary of each year's work in any given branch of physical science, and in facilitating orientation in the literature of any such branch, is now too widely recognized to need especial emphasis.

J. E. Trevor

A History of Physics in its Elementary Branches, Including the Evolution of Physical Laboratories. *By Florian Cajori. 14 × 21 cm; pp. viii and*

322. New York: The Macmillan Company, 1899. Price: cloth $1.60. — Mr. Florian Cajori, who is well known by his History of Mathematics, and his History of Elementary Mathematics, now appears with a compact treatise on the history of general physics. In the preface to the book he says: "The writer is convinced that some attention to the history of a science helps to make it attractive, and that the general view of the development of the human intellect, obtained by reading the history of science, is in itself stimulating and liberalizing." It is open to very little question that the best way to teach a scientific subject is to present an account of its historical development. And it may here be said at once that in writing an outline history of physics our author has produced a very interesting little book.

The first fifty pages of the history are made up of a brief description of the progress of physical science among the Greeks, the Romans, the Arabs, in the Middle Ages, and during the Renaissance. The remainder is devoted to the results of physical research in the XVII., the XVIII., and the XIX. centuries. An interesting essay on the evolution of the physical laboratory completes the whole.

The subject matter is well chosen, and is presented in a pleasant way. It is noticeable, too, that the subject is brought well down to date. An objection that might be made to the author's method is that in many cases important results are merely stated, no indication being given of the way in which they were reached. An example of this is the statement, on page 219, of Nernst's formula for the electromotive force of a voltaic cell. Such incoherent strings of facts make simply so much dead weight. They do not tend to foster an interest in the growth of science. Despite this occasional feature, however, the book is an interesting one; and it deserves to be widely read — as it probably will be. It may be worth while to mention, for the improvement of future issues, that Olszewski's name, on page 195, should not be spelled Olzewski; and that Nernst's first name is Walther, and not Walter, as on page 219. Proper names should be correctly spelled in a historical treatise if anywhere. *J. E. Trevor*

L'Industrie du Goudron de Houille. *By G. F. Jaubert. 12 × 19 cm; 172 pp. (Encyclopédie des Aide-Mémoire). Paris: Gauthier-Villars et Fils. Price: paper, 2.50 francs; bound, 3 francs.* — The treatment of the subject is popular in so far as this is possible; and the result is a very readable book, sufficiently accurate and detailed for the general reader for whom it is intended. This as well as the other publications of the *Encyclopédie Scientifique des Aide-Mémoire* can be highly recommended to those who wish an interesting, clear, and yet not too technical an account of the subjects treated.

W. R. Orndorff

The Year-Book for Colorists and Dyers. *By Harwood Huntington. Vol. I. 13 × 19 cm; 299 pp. New York: Harwood Huntington, 1898.* — The author states in the preface to this book that the need of a concise recapitulation of advances made annually in the special field worked in by dyers and colorists has long been felt. It is to supply this want that this year-book has been published. It contains a great deal of information in a small space, and will no doubt be of value to those engaged in the dyeing and allied industries.

W. R. Orndorff

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry

General

On the variation of energy in isothermal changes: On electric energy. *H. Pellat. Comptes rendus*, **125**, 699 (*1897*). — The heat dQ and the work $-dW$ added to a system of bodies in any reversible thermodynamic change may be represented as

$$dQ = a dT + b dx,$$
$$-dW = -h dT - k dx;$$

where T is the thermodynamic temperature, and x is an additional variable serving to define the state of the system. Combining these equations with

$$dU = J dQ - dW,$$
$$dS = dQ/T,$$

for the differentials of the energy and the entropy; writing the condition that these differentials are exact; and eliminating; one finds

$$b = \frac{T}{J}\left(\frac{\partial k}{\partial T} - \frac{\partial h}{\partial x}\right),$$

which is termed 'the generalized Clapeyron formula'. For isothermal changes of the energy we have

$$dU = (Jb - k)dx.$$

The quantity of heat bdx requisite to maintain the temperature constant when x changes is often replaced by $-kdx$, which is an error. By way of illustration, the proper calculation of the isothermal change of energy is made for the transfer of electricity from one plate to the other of a condenser. *J. E. T.*

A revision of the atomic weight of nickel, II. *T. W. Richards and A. S. Cushman. Proc. Am. Acad.* **34**, *327* (*1899*). — The nickel bromid used in the first research (**2**, 396) contained traces of sodium bromid. The work has been repeated determining both the nickel and the bromin. The most probable value is 58.706, which is undoubtedly accurate to within one ten-thousandth.

W. D. B.

A revision of the atomic weight of cobalt, II. *T. W. Richards and G. P. Baxter. Proc. Am. Acad.* **34**, *351* (*1899*). — The cobalt bromid previously analyzed (**2**, 396) contained traces of other bromids for which an accurate correction cannot now be given. Two new series gave 58.992 and 59.004 for cobalt,

the average being 58.998. The two previous series gave 58.995 and 58.987 uncorrected. For the present the authors prefer to take the mean of these four values 58.995, though they incline to the belief that the true value is almost exactly 59.000. *W. D. B.*

The use of vacuum as a means of preventing loss of heat. *A. Weinhold. Wied. Ann.* **66,** *544 (1898).* — This is a claim for priority in the use of the vacuum chamber as a means of preventing heat loss. The idea is claimed by d'Arsonval, but the author points out that he published an account of the method seven years previous, in 1881. *H. T. B.*

An apparatus called a hermetical pourer. *R. Personne de Sennevoy. Comptes rendus,* **126,** *224 (1898).* — By means of a pump with a plunger it is possible to draw liquid from a hermetically sealed vessel without letting in air. The apparatus is recommended for use with petroleum and other inflammable or volatile liquids. *W. D. B.*

On a source of error in the Andrews's method of measuring the specific heat of a liquid. *E. Gumlich and H. F. Wiebe. Wied. Ann.* **66,** *530 (1898).* — The method of calorimetry due to Andrews is similar to the better known method of Favre and Silbermann. Instead of introducing the liquid under experiment into the mercury bulb as in the latter, the mercury bulb is introduced into the liquid. In both cases the change in the volume of mercury for an observed change in temperature of water gives the heat equivalent of the stem. The source of error pointed out by the authors is so self-evident that it would seem absurd to go into the matter at all unless they had attempted to make a more careful study than they have done. The error is in the assumption that the same quantity of heat will be given up by the bulb to liquids whose end temperatures differ. The heat given up, as the authors point out, is not only dependent on the mean difference in temperature between the bulb and the liquid, but also on the total contraction of the mercury which is conditioned by the volume of the bulb.

In working with salt solutions at low temperatures this error would probably amount to considerable. The authors endeavor to determine the size of the error, but their errors of observation completely blind any conclusions they may have arrived at. The correction deduced by the authors amounts to about one in a thousand per degree difference in the end temperature of the liquid. Their errors of observation amount to nearly one percent, which is not surprising when their total rise of temperature is only 1.68° and they try to measure this with a mercury thermometer divided to tenths. *H. T. B.*

On a method for the estimation of the thermal conductivity of solid bodies. *F. A. Schulze. Wied. Ann.* **66,** *207 (1898).* — The method is very simple although the author rather blinds it with too profuse mathematical discussion. A metal rod considered of infinite length compared with its diameter is carefully enclosed for the most part in wadding in order to keep it during the experiment at an equable temperature. At a distance of from 4 to 10 cm, depending on the nature of the metal used, from one end left exposed, a thermocouple (iron-constantan) is placed in a small boring. At a given moment a stream of water

is allowed to play on the exposed end at a temperature different from that of the protected length of the rod. The change in the temperature of the thermocouple is noted by observing the change in the galvanometer reading. As the deflections pass through even scale readings the times are recorded on a chronograph. The deflections finally show that the temperature is approaching a steady state. By taking another series of observations with the stream of water at a different temperature the times are compared for the attainment of the same galvanometer deflection. From these two series of observations the thermal conductivity may be deduced by making the following assumptions: (1) The end face of the rod accepts momentarily the temperature of the stream of water; (2) That the galvanometer scale may be considered a temperature scale of equal parts for the thermocouple.

Taking θ_1, θ_2, t_1 and t_2 as the corresponding temperatures and times of equal scale deflections, then the coefficient of temperature conduction x may be calculated; for taking θ as the temperature indicated by the thermocouple, then

$$\theta = \frac{2\theta_1}{\sqrt{\pi}} \int_{\frac{x}{2\kappa\sqrt{t_1}}}^{\infty} e^{-q^2} dq$$

where x is the distance of the thermocouple from the end of the bar under the influence of the stream of water. Hence

$$\frac{2\theta_1}{\sqrt{\pi}} \int_{\frac{x}{2\kappa\sqrt{t_1}}}^{\infty} e^{-q^2} dq = \frac{2\theta_2}{\sqrt{\pi}} \int_{\frac{x}{2\kappa\sqrt{t_2}}}^{\infty} e^{-q^2} dq.$$

The author discusses mathematically the correctness of the two assumptions and works out small corrections that are necessary to be applied to the readings. He also works out the influence of the surrounding temperature on his results and finds it varies considerably with the time, from about two parts in 1000 for 8 seconds to 10 percent for one minute. He closes the paper by giving the results of his determinations on a copper rod 1 cm diameter and 35 cm long. The values of x deduced agree to about 3 percent, his mean value being 0.6108 gram-calories. *H. T. B.*

One-Component Systems

Measurements of vapor pressure, II. *G. W. A. Kahlbaum. Zeit. phys. Chem.* **26,** *577 (1898).*—The article presents in condensed form the results obtained by the author and five of his pupils during several years of work. When a liquid boils, the pressure in the retort is the same as that measured at the end of the condenser. The dynamical method of determining vapor-tensions is severely tested and is shown to yield satisfactory results. The author ably discusses the relative accuracy of vapor-tension measurements, and defends his method of interpolation by use of curves constructed on a large scale.

The boiling-points of the series of fatty acids (C_1 to C_{10}) were determined at a large number of pressures varying from 10 mm to 760 mm. A comparison of the results obtained with the boiling-points calculated from those of water and propionic acid by the use of Dühring's law showed only approximate agreement, the differences being greater when the comparison is made with the values deduced from water than when those derived from propionic acid are used. Dühring's law is therefore only approximate. When the differences between the boiling-points of the acids of this series are compared, it appears that in the case of formic and acetic acids and also nonoic and decoic acids the differences do not vary with the pressure, so that the boiling-point curves of each of these pairs are parallel. Divergence of the curves of acetic and propionic acids takes place as the pressure diminishes. In all other cases the curves converge as the pressure decreases.

The following are the boiling-points of nine benzene derivatives at 760 mm: benzene 80.3°, brombenzene 155.5°, benzaldehyde 178.3°, phenol 181.4°, anilin 183.9°, benzonitrile 190.6°, benzyl alcohol 205.0°, nitrobenzene 208.3°, benzoic acid 249.0°. At 6 mm the boiling-points are: bromobenzene 32.5°, benzaldehyde 53.0°, benzonitrile 59.9°, anilin 60.5°, phenol 65.3° nitrobenzene 76.1°, benzyl alcohol 83.9°, benzoic acid, 121.2°. Thus intersection of the boiling-point curves occur in the following cases: benzonitrile-phenol, benzonitrile-anilin, anilin-phenol, benzyl alcohol-nitrobenzene. Previously the only known case of intersection of boiling-point curves was that of ethyl alcohol-benzene.

The boiling-points of anilin and its methyl, ethyl, dimethyl and diethyl derivatives were determined at pressures ranging from 5 mm to 760 mm. The boiling-point curves of anilin and dimethyl anilin converge as the pressure diminishes, as do also those of methyl and ethyl anilin; but those of methyl and diethyl anilin diverge. This makes the curves for anilin and methyl anilin and again those for dimethyl and ethyl anilin parallel.

Boiling-point determinations (at pressures varying from 1 mm to 760 mm) of acetophenone, benzoyl chlorid, and methyl benzoate show that Schroeder's rule that substitution of the groups $CO.CH_3$, $COOCH_3$, and COCl for H produce the same changes of boiling-point is untenable, since though the difference in boiling-points of the last two compounds is 0.4° at 760 mm, it is 3.5° at 10 mm. Again, the difference in the boiling-points of the first two compounds is 4.4° at 760 mm and 5.2° at 10 mm, and the difference between the boiling-points of the first and third is 4.0° at 760 mm and 1.7 at 10 mm.

The boiling-points of the three cresols, the three toluidins, *o*- and *p*-dimethyl toluidins, and *o*- and *p*-nitrotoluenes were determined at various pressures. Paracresol boils 0.5° higher than the meta and 11.2° higher than the ortho compound; this holds for all the pressures investigated. The boiling-point curves are therefore parallel. The same is true of those of the toluidins, so that Dalton's law holds for both of these groups of compounds. This law does not hold for the dimethyl toluidins or the nitrotoluenes; and since there is a considerable difference between the boiling-points of these substances, the law of Dalton probably holds good only for substances whose boiling-points lie close together.

The boiling-point curves of trimethylene bromid and propylene bromid

diverge with increase of pressure, as do also those of ortho- and metachloranilin. The curves of chloro- and bromonaphthalene converge as the pressure diminishes, the differences in the boiling-points being 21.8° at 760 mm and only 8.8° at 2 mm. The generally accepted relations existing between chemical composition and boiling-points really do not have much significance, since when the comparisons are made at pressures other than 760 mm other relations are found. For the whole range of pressures, substitution in benzene derivatives causes a greater change in the boiling-point than in toluene derivatives. With a few exceptions the boiling-point curves of simpler aromatic compounds are flatter than those of the more complex compounds. This the author ascribes to greater cohesion of the simpler molecules. Generally fatty compounds have flatter curves than aromatic compounds of nearly the same boiling-point. No curve of an aromatic compound runs even approximately parallel to that of a fatty compound. The exceptions to this rule are that the curves of toluene and isocapronic acid are parallel, as are also those of benzoic and *n*-pelargonic acids. Within the aromatic series and also within the fatty series parallelism of boiling-point curves frequently occur. The OH group in compounds seems to cause flatness of the boiling-point curve.

The molecular dispersion as deduced according to the formula of Lorenz (between H_α and H_γ) in many cases increases as the boiling-point increases (comparisons were made for the pressure interval 10 mm to 760 mm). There are apparently many exceptions to this rule; so in the series of the fatty acids, the molecular dispersion continues to increase though the boiling-point change is nearly constant. The author desires simply to point out this relation, further elaborations and explanations are to follow. *L. K.*

On the elevation of melting-point by pressure and the continuous transition from the solid to the liquid state. *A. Heydweiller. Wied. Ann.* **64,** *725 (1898).* — With a view of finding some experimental evidence for the existence of critical phenomena between the liquid and solid states, the author melted various substances in sealed capillaries, the expansion accompanying fusion supplying the required pressure. In one case (diphenylamin) an elevation of melting-point of as much as 70° was reached, for which the pressure 3500 atmospheres was computed. The only result which pointed in any way to a critical phenomenon was the peculiar behavior of menthol. At ordinary pressures this substance, besides solidifying to an opaque mass, turns transitorily into a transparent solid. In the capillary, one end of which was cooled, the transition from the transparent solid to the liquid appeared to be gradual. [See **3,** 114]. *F. B. K.*

An estimation of the coefficient of pressure and of the difference between the coefficients of expansion and pressure of air. *W. Hoffmann. Wied. Ann.* **66,** *224 (1898).* — In the determination of the coefficient of pressure for air the author uses the constant volume Jolly air thermometer, but in order to make the readings independent of the variations in the air pressures he replaces the open mercury column by a barometric tube, thus leaving the air in the bulb only under the pressure of the mercury in the barometer tube. His mean determination gives

$$\alpha_p = 0.0366957.$$

The observations appear to agree to about 4 in 10000. In determining the difference between the coefficients of pressure and volume the author designs a special air thermometer from which three sets of readings give data for calculating both the coefficients. The special advantage is that the same steam reading is used in calculating both coefficients, and hence errors in determining the more difficult point eliminated on the difference. The author's method is to introduce between the bulb and the Jolly air thermometer (V) and the barometer tube a smaller pear-shaped bulb (V_1) such that

$$V_1(1+\alpha 100) = V\alpha 100.$$

Then, having suitable marks above and below the bulb V_1, the readings are

Lower mark V in steam
" " V_1 " ice
" " V " "
" " V_1 " "
Upper mark V " " .

The mean result of the determinations neglecting an observation which the author considers faulty gives

$$\alpha_v - \alpha_p = 0.00000123. \qquad H.\ T.\ B.$$

On the rigorous determination of the molecular weights of gases, starting from their densities and the variations of these from the law of Mariotte. *D. Berthelot. Comptes rendus*, **126**, *954, 1030 (1898).*—The variation ϵ, from the gas laws at atmospheric pressure, may be represented by the formula

$$\epsilon = \frac{p_0 v_0}{pv} - 1 = \alpha(p - p_0),$$

where α is a constant for pressures varying from one to six atmospheres. If we express p in atmospheres and call p_0 unity we shall have for the molecular volumes of two gases $\frac{v'_0}{v''_0} = \frac{1-\alpha'}{1-\alpha''}$. If d', d'', etc., are the densities under atmospheric pressure at the temperature of the experiment the molecular weights are proportional to $(1-\alpha')d'$, $(1-\alpha'')d''$., etc. Taking the molecular weight of oxygen as 32 the author calculates the following atomic weights: H = 1.0074; N = 14.007; C = 12.007, the value for carbon being obtained from the data for carbon monoxid. In the second note, it is pointed out that these data agree admirably with those obtained by purely chemical processes. *W. D. B.*

On the substances associated with argon. *W. Ramsay and M. W. Travers. Zeit. phys. Chem.* **27**, *564 (1898).*—The fractional distillation of liquid argon by means of boiling air led to the separation of two new materials. The first fraction of the gas was mixed with oxygen and sparked over sodium hydroxid solution. A gas was obtained with new characteristic red spectrum lines and a density of 14.67. The authors consider this to be a mixture of argon and a new gas, "neon", with a density of 10 or 11. Near the end of the fractionation a white solid was left in the vessel, which at ordinary temperatures is a gas of practically the same density as argon. It has a characteristic spectrum and the ratio of its specific heats is 1.660. The name 'metargon' is suggested.

F. B. K.

On the probable occurrence of an unknown substance in the atmosphere. *O. Neovius. Wied. Ann.* **66,** *162 (1898).* — By comparing the red argon spectrum with the spectrum of nitrogen between the values of λ 3700 and 5000, the author finds three coincident lines, which he believes to be merely due to chance. A comparison of the blue argon spectrum, however, shows some thirty-four coincident lines, which he thinks cannot be due to chance, but to a hitherto unknown substance present in both the nitrogen and argon. He divides his comparisons into three groups :

Group I.	Strong argon lines	
	Weak nitrogen	"
" II.	Strong nitrogen	"
	Weak argon	"
" III.	Weak nitrogen	"
	Weak argon	"

It is to the third that he attaches the most significance, for the coincidence in I may be due to the presence of the argon in the nitrogen, also those in II may be due to the trace of nitrogen impurity in the argon. In III, however, he does not think the coincidences can be set down to either the argon or the nitrogen. Since they belong to the weaker or even to the weakest of the lines observed in the argon spectrum they would not be visible in the weak nitrogen spectrum in which they occur with nearly the same intensity as in the pure argon spectrum. The author claims also that it is still less admissible, "*aus leicht ersichtlichen Gründen*", to accept that the lines belong to nitrogen. Hence belonging neither to nitrogen nor to argon they must belong to some unknown substance. The effect of the electrodes (copper) is eliminated by comparing the spectra of

N	-	-	-	sun	O	-	-	-	sun
N	-	-	-	air	O	-	-	-	air

and taking the lines common to all as due to the copper. The author uses for apparatus a small spectrometer with two Steinheil prisms. Photographic records are made of the spectra giving, as is claimed, an accuracy of 1/10 Angström unit. Apparently the author made no measurements of the red or blue argon spectrum himself, but his nitrogen spectra are compared with the argon given by Kayser, Eder and Valenta, and Crookes. A comparison of the spectrum of Krypton shows a coincidence for the line 4736. No known coincidence could be found in the Neon spectrum. A comparison of the metargon lines given by Baly with the carbon lines of Kayser show a close similarity, and also that for the most part these lines are outside the range of the new substance. The author thinks this new hypothetical element is present in the atmosphere to about the same extent as argon. He claims that Kayser's argon must have had about 50 percent of this substance. *H. T. B.*

On the measurement of high temperatures. *D. Berthelot. Comptes rendus,* **126,** *410, 477 (1898).* — The method consists in measuring the change in the index of refraction of a gas and the evaluation of the temperature depends upon the law that the change in the index of refraction of a gas is the same whether the change of density is effected by the change of pressure or of temperature. The author finds 962° for the fusing point of silver and 1064° for that of gold.

W. D. B.

On the specific heat of a metal at low temperatures. *U. Behn. Wied. Ann.* **66,** *237 (1898).* — As the specific heat of metals is tolerably well known for temperatures above 0°, the author points out the interest attaching to an investigation carried out at low temperatures, and goes on to describe some measurements made by himself for the metals Al, Fe, Ni, Cu, Pb, Pd, Ir and Pt between room temperature and — 80°, and — 186°.

His method is the usual method of mixture, with water as the mixing liquid. Having cooled the metal, suspended by a silk thread in an enclosed vessel, to — 80° with solid CO_2 and absolute alcohol or to 186° with liquid air, it is frequently withdrawn to the calorimeter. The coating of ice that is formed is quickly melted. The fall in temperature of the calorimeter is determined by means of a mercury thermometer reading to hundredths and generally amounted to 2.5 degrees. The temperature of the cold bath was taken with a thermocouple (iron constantan).

The sources of error mentioned by the author are:

(*a*) Impurity of the metals;

(*b*) Acceptance by the metal of the temperature of the cold bath;

(*c*) The transfer of the metal from the cold bath to calorimeter;

(*d*) Thermometer and thermocouple.

Error (*a*) was avoided by chemical examination. Error (*b*) by leaving the metal a sufficient length of time in the cold bath (one hour), determined by a special experiment on a copper cylinder in which a second thermocouple was placed. Error (*c*) was corrected for by determining experimentally the rate of gain in heat when the copper with the thermocouple embedded was taken out of the cold bath. Error (*d*) by comparing the mercury thermometer with a Reichsanstalt standard and accepting the formula for the thermocouple given by Holborn and Wien. The author notes that he uses wire from the same lot that Holborn and Wien used in their experiments. The result of the work shows that the specific heat decreases with decreasing temperature, the more the higher the specific heat. The author suggests that from a consideration of the plots of the different metals between 100° and — 186° the curves would converge towards the absolute zero, showing an equal and very small specific heat.

H. T. B.

Two-Component Systems

Contribution to our knowledge of metallic alloys. *M. Herschkowitsch. Zeit. phys. Chem.* **27,** *123 (1898).* — The author has measured the electromotive force of various amalgams against one of the pure metals. Four classes are distinguished. Each metal crystallizes by itself. In this case the potential of the amalgam will always be that of the less noble metal. Two series of solid solutions are possible. In this case the potential will vary continuously as long as only one phase is present and will remain constant so long as there are two solid phases present. A continuous series of solid solutions is possible in which case the potential will vary continuously. One compound is possible and no solid solutions. There will then be a sudden change of potential when the less noble metal disappears, and the potential will then be that of the compound. It is to be noticed that this classification is very incomplete and it would have

been much better if the author had looked up the classifications of Retgers, and of Roozeboom, which are much more satisfactory than that of Ostwald.

With cadmium and bismuth all mixtures showed the potential of pure cadmium. With cadmium and tin all mixtures having more than three percent of cadmium give the value for cadmium. With more dilute mixtures the potential drops off rapidly implying that cadmium is somewhat soluble in solid tin. The same phenomenon occurs with cadmium and lead. With zinc and tin the value drops suddenly, remains constant over a wide range of concentrations and then falls off gradually, showing the existence of two sets of solid solutions. With zinc and copper the values are at first nearly constant and then drop off rapidly to the values for copper. The author interprets this as showing the existence of a compound Zn_2Cu ; but the experimental data as published point rather to the existence of two sets of solid solutions, zinc being very soluble in copper and copper sparingly soluble in zinc. Zinc and bismuth are apparently each slightly soluble in the other. The data for zinc and silver are interpreted by the author as showing the existence of a compound Zn_4Ag ; but the fact that values approach the value of pure silver would seem to negative this conclusion and the assumption of two sets of solid solutions would again appear to account for the phenomena. With zinc and antimony the order appears to be solid solution of antimony in zinc, the compound $ZnSb_2$, and then practically pure antimony. The author accounts for the phenomena with tin and Cu and with tin and silver by assuming the existence of Cu_3Sn and of Ag_4Sn respectively. It is not clear however why Cu_3Sn should have the same potential as pure copper. Silver and copper appear to form a continuous series of solid solutions. Curiously enough tin and antimony were not studied, though Küster has shown that these form a continuous series of solid solutions. No attempt is made to compare the results obtained from the measurement of the electromotive forces with the results obtained from the freezing-point determinations of Heycock and Neville and of others.

The second part of the paper contains measurements of heats of formation of alloys. The general result is summed up by the author in the statement that the heat of formation is sometimes positive and sometimes negative, even in cases where compounds are formed. *W. D. B.*

The transition temperature of sodium sulfate. A new fixed point in thermometry. · *T. W. Richards and J. B. Churchill. Zeit. phys. Chem.* **26**, *690 (1898).* — The transition temperature of the change $Na_2SO_4 10H_2O$ to $Na_2SO_4 + 10H_2O$ is found to be very suitable as a fixed point in thermometry. The temperature at which the change takes place is found by careful examination to be 32.484° C, which is 32.379° on the hydrogen scale. This temperature lies near the point of maximum difference of the two scales. Sodium sulfate of requisite purity can easily be obtained, two recrystallizations in porcelain dishes of the C. P. commercial article being sufficient to insure the degree of purity required. A very constant temperature is obtained if the melting-point of Glauber's salt is taken. Ordinary changes of pressure have so slight an effect that they may be neglected. No unusual precautions need be taken to obtain results that are correct to 0.01°. It is thought that other transition temperatures can likewise be accurately determined and that they will be useful in thermometry. *L. K.*

The compound of ammonium nitrate with ammonia. *E. Divers. Zeit. phys. Chem.* **26,** *430* (*1898*). — Attention is called to the fact that the recent experiments of Kuriloff have confirmed the results obtained by the author in 1872. *W. D. B.*

The mutual solubility of liquids and the critical point of solubility. *V. Rothmund. Zeit. phys. Chem.* **26,** *433* (*1898*). — The mutual solubility of twelve pairs of liquids is investigated according to the method of Alexejew. The general conclusions reached are as follows: In eleven cases critical temperatures of solubility were found; and in the one case in which such a point could not be reached, the direction of the curve indicates that such a curve probably does exist. In nine cases critical temperatures were found *above* which complete miscibility occurs; in two cases critical temperatures were found *below* which the two phases cannot coexist. In several instances the curves show a minimum in the lower arm and sometimes also a maximum in the upper arm, from which the author seems inclined to infer that all solubility curves are closed. Theoretical considerations are given to show that a continuous, closed solubility curve does exist. The law of the rectilinear diameter, the application of which could be foreseen from the analogy to the phenomena of the critical state, holds in the case of all those solubility curves that have an upper critical temperature of miscibility The equation of van der Waals in which pressure, volume and temperature are expressed in terms of their critical values can in general not be applied to solutions. The investigation of the difference in solubility in the liquid and solid states shows that two cases are here to be distinguished; the solubility curve either intersects or does not intersect that of the liquid. In the former case melting of the solid under the solvent may occur; in the latter case two layers of liquids that are in equilibrium with each other are always metastable. When the liquids are arranged in the order of their solubility in water, it appears that this order is the same as that obtained when they are arranged according to their dielectric constants. Acetic acid, isobutyric acid, isobutyl alcohol and furfurol are notable exceptions to the rule. *L. K.*

Combination of organic bases with different salts of oxygen acids. *D. Tombeck. Comptes rendus,* **126,** *967* (*1898*). — The sulfates of magnesium, zinc, cadmium and copper crystallize with two of anilin, the sulfate of cobalt with four and that of nickel with six of anilin. The nitrates of magnesium, zinc and cadmium also crystallize with two of anilin. *W. D. B.*

On the dissociation of selenium hydrid. *H. Pélabon. Zeit. phys. Chem.* **26,** *659* (*1898*). — At temperatures below 320° the limiting concentrations in the vapor phase reached by heating hydrogen and liquid selenium differ from those reached by heating selenium hydrid. With falling temperature the percentage decomposition of selenium hydrid first increases a little and then decreases rapidly. The percentage formation of selenium hydrid from hydrogen and selenium decreases rapidly with falling temperature, becoming practically zero at about 240°. Above 320° there is reversible equilibrium, the percentage decomposition of selenium hydrid decreasing as the temperature rises to 570° and increasing as the temperature rises beyond 570°. The paper also contains a very

interesting discussion on the different results obtained by sudden and by slow cooling from high temperatures and a study of the behavior of the system when heated unequally. *W. D. B.*

On the combinations of pyridin and of trimethylamin with formic and acetic acids. *G. André. Comptes rendus*, **126,** *1105 (1898).* — A mixture of pyridin and acetic acid can be obtained which boils at 150°–151°; mixtures of trimethylamin with formic or acetic acid give higher boiling-points than either of the components. The author looks upon the mixtures with constant boiling-points as compounds. With dimethyl anilin and acetic acid all mixtures boil at temperatures between the boiling-points of the components. *W. D. B.*

Note on the dissociation of water. *R. A. Lehfeldt. Zeit. phys. Chem.* **27,** *94 (1898).* — Referring to Luther's calculations of the concentration of free oxygen and hydrogen in water vapor, Ibid. **26,** 317, the author utters a warning to Dr. Luther and "all others who obtain extravagantly small numbers from the measurement of electromotive force" of the danger of drawing conclusions, quite inaccessible to experimental verification, from the laws of physical chemistry. But does not Mr. Lehfeldt run a still greater danger when he says "all theoretical considerations founded on the kinetic theory of gases — considerations of pressure, osmotic pressure, electromotive forces (which result from atomic charges)—have a statistical (statical?) character and it is impossible to imagine any statistical effect produced by molecules at such great distances from each other"? *F. B. K.*

On mixtures of gases. *A. Leduc. Comptes rendus*, **126,** *218 (1898).* — Instead of the statement that the pressure of a mixture of gases is equal to the sum of the pressures that each gas would exert if present by itself, the author proposes the statement that the volume occupied by a mixture of gases is equal to the sum of the volumes that each gas would occupy under the total pressure. For ideal gases the two statements are identical; but for actual gases the second is said to be more accurate. *W. D. B.*

On the law of the mixture of gases. *P. Sacerdote. Comptes rendus*, **126,** *338 (1898).* — Leduc's formulation of the law for mixtures of gases (preceding review) has been tested for mixtures of carbonic acid with nitrous oxid and with sulfur dioxid. The results were satisfactory. *W. D. B.*

On the composition of air in different places and on the density of gases. *A. Leduc. Comptes rendus*, **126,** *413 (1898).* — Contrary to the results of Lewy the author finds that the amount of oxygen in the air varies with the season, the altitude, the neighborhood of the sea and, possibly, with the latitude. It is proposed to refer the densities of gases to that of oxygen as unity. *W. D. B.*

Poly-Component Systems

The application of the theory of equilibrium to the formation of oceanic salt deposits with special reference to those at Stassfurt. *J. H. van't Hoff and W. Meyerhoffer. Zeit. phys. Chem.* **27,** *75 (1898).* — This paper contains a study of the equilibrium between magnesium chlorid and water at different temperatures. Six hydrates have been isolated, with twelve, eight, six, four

and two of water, the one with eight of water occurring in two modifications, of which one, the β form, can never exist in stable equilibrium with solution and vapor. The following stable quadruple points were determined: ice and $MgCl_2 12H_2O$ at $-33.6°$; $MgCl_2 12H_2O$ and $MgCl_2 8H_2O\alpha$ at $-16.8°$; $MgCl_2 8H_2O\alpha$ and $MgCl_2 6H_2O$ at $-3.4°$; $MgCl_2 6H_2O$ and $MgCl_2 4H_2O$ at $116.7°$; $MgCl_2 4H_2O$ and $MgCl_2 2H_2O$ at 181°–182°. It was not possible to work above 186° owing to the evolution of hydrochloric acid. The hydrate with twelve of water melts at $-16.4°$. The following labile quadruple points were found: ice and $MgCl_2 6H_2O$ at about $-50°$ (by extrapolation); $MgCl_2 12H_2O$ and the hexahydrate at $-19.4°$; $MgCl_2 12H_2O$ and $MgCl_2 8H_2O\beta$ at $-17.4°$; $MgCl_2 8H_2O\beta$ and the hexahydrate at $-9.4°$. In addition there are numerous quantitative determinations of points on the boundary curves. *W. D. B.*

Experiments on the solubility of the carvoximes. *H. Goldschmidt and H. C. Cooper. Zeit. phys. Chem.* **28,** *711 (1898).* — The possibility that dextro and laevo modifications of an optically active compound, which are soluble to the same extent in inactive solvents, might have different solubilities in optically active solvents was suggested by van 't Hoff. Accordingly the solubilities of dextro, laevo and inactive carvoximes in dextro limonin were tested. The result was that the dextro and laevo modifications show no difference in solubility. Liquefied inactive carvoxime (i. e. the racemic mixture) was soluble to the same extent as the dextro variety, but the *solid* inactive mixture had a solubility different from that of the dextro compound. This shows that in the liquid state the inactive compound is only a mechanical mixture of the dextro and laevo varieties, so that the racemic condition really only has significance when the mixture is in the solid form. Rapid crystallization of the inactive compound from solution or from the molten state apparently yields a mixture of crystals of the dextro and laevo varieties which after a time change to the racemic form. *L. K.*

Action of calcium sulfate on some alkaline halids. *A. Ditte. Comptes rendus,* **126,** *694 (1898).* — When potassium chlorid is added continuously to a solution saturated with respect to calcium sulfate, there comes a point at which the double sulfate $K_2SO_4CaSO_4 4H_2O$ crystallizes. Some analyses are given of the solutions along the 21° isotherm; but the nature of the solid phases is ignored. The same phenomena occur when the bromid or the iodid of potassium is substituted for the chlorid. With ammonium chlorid no double sulfate is formed and one is not obtained with sodium chlorid. The author is much handicapped by his ignorance of the phase rule. *W. D. B.*

On the causes of the reciprocal displacement of two acids. *A. Colson. Comptes rendus,* **126,** *831 (1898).* — From the text it is impossible to make out what the author has actually observed. Only this much is clear: At 12° hydrogen sulfid is not completely absorbed by Ag_3PO_4, while it is at higher temperatures. Since the reaction is exothermal, this behavior is unintelligible unless the author has been studying a case of false equilibrium. *W. D. B.*

Influence of temperature on chemical reactions. *A. Colson. Comptes rendus,* **126,** *1136 (1898).* — At 10° hydrogen sulfid does not act perceptibly on dry $Zn_3(PO_4)_2$; but decomposition takes place at 100°, rapidly at 160°. The

mass of hydrogen sulfid decomposed in the unit of time is proportional to the square of the pressure. Even at 0° hydrogen sulfid reacts with cupric orthophosphate or pyrophosphate, though very slowly. *W. D. B.*

On the formation of the carbids of the alkalies, of the alkaline earths, and of magnesium. *H. Moissan. Comptes rendus*, **126**, *302 (1898)*. — Sodium acts very slowly on acetylene, evolving hydrogen and forming the compound C_2HNa. On heating this substance acetylene is given off and the carbid C_2Na_2 is left behind. Heating still higher the metal escapes leaving graphite behind. Potassium and lithium carbids can be obtained in the same way. Magnesium carbid breaks up below the fusion point of magnesium. The reason that the carbids of potassium, lithium, sodium and magnesium cannot be prepared in the electric furnace is that the temperature of the latter is too high. *W. D. B.*

On the dissociation of the carbids of barium and manganese. *Gin and Leleux. Comptes rendus*, **126**, *749 (1898)*. — The authors have succeeded in driving off barium and manganese from the carbids of these metals in the electric furnace. The carbon remains. *W. D. B.*

On the relation between the reduction by nascent hydrogen, the electrolysis and the photolysis of carbonic acid. *A. Bach. Comptes rendus*, **126**, *479 (1898)*. — Formaldehyde is formed when aqueous carbonic acid is acted on by hydrogen and palladium. The same product is obtained by the action of sunlight and the author feels sure that it might also be obtained by electrolysis. *W. D. B.*

On the separation and determination of iodin, bromin and chlorin. *A. Carnot. Comptes rendus*, **126**, *187 (1898)*. — Iodin is set free by sulfuric acid and nitrous vapors; it is then removed with carbon bisulfid. Bromin is set free with chromic acid and removed with carbon bisulfid. *W. D. B.*

On the sterilization of liquids by filtration. *J. Hausser. Comptes rendus*, **126**, *844 (1898)*. — If infusorial earth be heated at a temperature a little below that at which it fuses, it acquires very marked absorbent properties. *W. D. B.*

Osmotic Pressure and Diffusion

Effect of the X-rays on the phenomenon of osmose. *H. Bordier. Comptes rendus*, **126**, *593 (1898)*. — When the X-rays passed down through a solution of cane sugar to the membrane, the rate at which water diffused into the solution was reduced very decidedly. The same effect was produced when a bit of aluminum foil was placed between the source of the rays and the solution. Unfortunately it did not occur to the author to reverse the position of the solution and the solvent and see whether the rate of diffusion was increased. The suggestion is made that the action of the X-rays upon living tissue may be connected with a disturbance of osmotic equilibrium. *W. D. B.*

Osmotic experiments on very dilute solutions of cane sugar. *A. Ponsot. Comptes rendus*, **125**, *867 (1897)*. — Reviewed (**2**, 203) from Bull. Soc. Chim. Paris, (3) **19**, 9 (1898).

Study of physical and chemical equilibria by the osmotic method. *A. Ponsot. Comptes rendus*, **126**, *335 (1898)*. — A statement to the effect that the study of chemical and physical equilibria can be simplified by assuming the

existence in the solution of a number of boxes semipermeable with respect to different components, each box being provided with its own piston.

W. D. B.

On the diffusion of gases through gelatine containing water. *A. Hagenbach. Wied. Ann.* **65,** *673 (1898).* — The diffusion of gases through a solid solution of twenty percent gelatine in water in presence of an excess of the latter is investigated. For a description of the apparatus and method the original article must be consulted. At 14° to 15° and with a difference in pressure of one atmosphere, the following volumes of gas expressed in cubic centimeters at 0° and 760 mm pass through a cube having an edge of one cm of the gelatine solution in one day: CO_2 0.845, N_2O 0.509, H_2 0.0565, H_2S 3.96, O_2 0.230, NH_3 1271. The coefficients of absorption of these gases in the gelatine solution were also determined. They were found to differ but slightly from Bunsen's results for water, — the percentage differences are greater at low temperatures. Calculation of the diffusion constants K by dividing the above volumes by Bunsen's coefficients of absorption of the gases by water gives the following results: CO_2 at 15° 0.843, at 0° 0.770, N_2O at 14° 0.634, H_2 at 14° 2.95, H_2S at 15.5° 1.24, NH_3 at 17° 1.594, O_2 at 14° 7.58. The author apparently inclines to the view that the relatively high value for oxygen is due to chemical action of this gas on gelatine. He hopes to investigate this further. A comparison of these diffusion coefficients with those found by Hüfner for water shows that the former are smaller throughout with the (possibly only apparent) exception of oxygen. The results obtained indicate that Exner's law that the volumes of the diffusing gases are to each other as their coefficients of absorption and inversely as the square roots of their densities is only approximate. *L. K.*

Velocities

The rate of hydrolysis of maltose. *A. von Sigmond. Zeit. phys. Chem.* **27,** *385 (1898).* — The article contains polarimetric measurements of the rate of the above reaction in the presence of hydrochloric, sulfuric and oxalic acids. The reaction is monomolecular and obeys the same temperature law as cane sugar. The rate is however much less than in the case of the latter substance.

F. B. K.

Effect of the concentration on the reaction velocity. *A. v. Hemptinne. Zeit. phys. Chem.* **26,** *728 (1898).* — The reaction was the formation of iodin in acidified solutions of potassium iodid. For dilute solutions of potassium iodid the reaction is bimolecular. With double normal solutions of sulfuric acid a satisfactory constant was obtained, but this was not the case with fifty and eight percent solutions of acetic acid. The action of light increases the reaction velocity and the effect due to the change in the strength of the light is about the same no matter what the acid. The catalytic action of oxalic and acetic acids is much greater than would be expected from the conductivity. With increasing concentration of acetic acid the reaction velocity increases up to a maximum for seventy percent acetic acid. The action of concentrated acids on metals is also very different from the action of dilute acids. This paper is merely a preliminary study. *W. D. B.*

Catalytic action on the speed of oxidation of sodium sulfite by the oxygen of the air. *S. L. Bigelow. Zeit. phys Chem.* **26,** *493* (*1898*). — Air is passed through an aqueous solution of sodium sulfite, the strength of which is determined from time to time with a standard solution of iodin with the aid of a solution of sodium thiosulfate. The effect of the addition of various substances — chiefly organic — in small amounts on the rate of oxidation is tested. With the exception of succinic acid, carbonic dioxid and ozone — which accelerate the speed of the reaction — the substances tested either retarded the reaction or had no effect. The latter substances are ethyl acetate, acetone and sodium sulfate. The substances that had a retarding influence include primary and secondary alcohols, polyatomic alcohols, phenol, the three cresols, anilin, ether, acetic- and benzaldehydes, benzene, turpentines, sodium hydroxid, potassium tartrate and sodium succinate. Many difficulties had to be overcome in order to obtain reliable results; and yet after all different samples of water from the same source always yielded very different results, a fact for which no explanation is found.

The retardation of the speed of oxidation of sodium sulfite by the substances named the author terms catalytic action. The only reason that he gives for doing so is that considerable retardation is caused by small amounts of substance. In no case does he show that the substance that causes such retardation remains unchanged or — that being difficult to do — that a little of it will suffice to retard the reaction for a considerable period of time, the experiments being run generally only for thirty minutes.

Now the substances that retard the oxidation are, with the exception of sodium hydroxid, reducing agents; and indeed the order in which the author arranges the substances as to their retarding influence is, very nearly at least, that of their reducing power. The substances that did not retard are not reducing agents or but very poor ones. In the face of these facts it would at least appear doubtful as to whether the retardation of the oxidation by these various ingredients is really catalytic action. *L. K.*

On the catalytic action of platinum black. *A. von Hemptinne. Zeit. phys. Chem.* **27,** *429* (*1898*). — In the hope of throwing more light on the question as to whether the occlusion of hydrogen by platinum black is due to chemical combination or to surface condensation, the author makes comparative measurements of the absorption at ordinary and at very low temperatures. Chemical combination would probably be checked by great cold: condensation on the other hand would be increased. As a matter of fact charcoal was found to condense about six times as much hydrogen at −78° as at 15°, while in the case of platinum black the absorption was much *less* at the *low* temperature. The author, therefore, rejects the assumption of simple surface condensation as the cause of the absorption of hydrogen by platinum black. He obtains several curious results with hydrogen and carbon monoxid in palladium, but refrains from drawing conclusions until more detailed experiments shall have been carried out in boiling air. *F. B. K.*

Note on the rate of dehydration of crystallized salts. *T. W. Richards. Zeit. anorg. Chem.* **17,** *165* (*1898*). — Reviewed (**2,** 403) from Proc. Am. Acad. **33,** 23 (1897).

On the dispersion of electrically glowing platinum and palladium wire. *W. Stewart. Wied. Ann.* **66,** *88 (1898).* — The author investigates the phenomenon first pointed out by Nahrwold that platinum heated to a red heat by an electric current apparently sends off fine particles. He also undertakes a study of palladium wire as well as platinum in air, hydrogen, nitrogen, and in oxygen of different pressures.

His method is to suspend a wire of about 0.25 mm diameter and 170 mm long between two large platinum hooks soldered to copper leads. By enclosing the wire in a suitable vessel he is able to introduce the different gases and to maintain them at different pressures. The temperature of the wire is kept constant at any desired point for all the experiments by measuring the differences of potential between the copper leads and a suitable manganin resistance. The weight of the wire before and after the experiment gives the amount of the dispersion.

The results of the work are :

1. The strength of the dispersion decreases for both Pt and Pd the longer the wire is kept glowing. The weight lost varied from 0.68 percent to 0.11 percent after the sixth experiment.

2. The dispersion is the same for dry air as for moist air.

3. The dispersion is unchanged if the wire is surrounded by a brass tube connected to earth.

4. With decreasing air pressure the dispersion of the Pt decreased while that of the Pd increased.

5. In hydrogen there was no dispersion of the Pt even at a clear white heat. The Pd shows only about one-sixth the effect produced by air.

6. In nitrogen the metals show only a very weak dispersion.

7. That the dispersion in air is conditioned by the presence of oxygen.

H. T. B.

Electromotive Forces

On galvanic polarization. *H. Jahn. Zeit. phys. Chem.* **26,** *385 (1898).* — The author has determined and tabulated the polarization at 0° and at 40° ; the temperature coefficient of the polarization ; the loss of heat in the battery during the decomposition of one reacting weight of the salt at 20° ; the heat effects at 20° in the decomposition cell at the anode and the cathode for the sulfates of copper, zinc and cadmium and for the nitrates of copper, lead and silver. The battery used was the modified De la Rue cell (**2,** 205) and the measurements were made with the ice calorimeter. Thermodynamic formulas are deduced for the polarization with salts of the heavy metals and with acids. The value of these formulas is open to question. For instance, the conclusion is reached that with an oxygen acid the polarization is independent of the concentration and dissociation of the acid. This is true only to the extent that the electromotive force of the hydrogen-oxygen gas cell is independent of the concentration and dissociation of the acid. This is very nearly the case, so nearly as not to be detected readily in polarization experiments ; but that is not a justification for the formula being wrong. Some experiments were also made with dilute solutions of the salts of the alkali metals. *W. D. B.*

On the thermal mercury ammeter. *C. Camichel. Comptes rendus*, **126**, *240* (*1898*). — Some modifications in the instrument previously described (**2**, 73). *W. D. B.*

On the mercury thermal ammeter, its industrial applications; a new standard of electromotive force. *C. Camichel. Comptes rendus*, **126**, *1028* (*1898*). — A further discussion of the accuracy of the new form of mercury ammeter (see preceding review). It is pointed out that by introducing suitable resistances the instrument can be used to measure potential differences. *W. D. B.*

Electrolysis and Electrolytic Dissociation

Preparation of glucinum by electrolysis. *P. Lebeau. Comptes rendus*, **126**, *744* (*1898*). — Glucinum can be precipitated electrolytically from the fused double fluorid GF_2NaF. The current was 6–7 amperes and the potential difference 35–40 volts. *W. D. B.*

On the alleged decomposition of sulfur. *H. Alexander. Zeit. Elektrochemie*, **5**, *93* (*1898*). — The author has repeated the experiments of Gross (**1**, 620; **2**, 140; **3**, 64). On the action of the current on molten silver chlorid and sulfid. No "bythium" was obtained. *W. D. B.*

The velocities of electrical ions at 18° in dilute aqueous solutions up to tenth-normal concentrations. *F. Kohlrausch. Wied. Ann.* **66**, *785* (*1898*). — One object of this paper is to test the assumption that the migration velocity of an ion may be treated as a function of the concentration, disregarding the dissociation completely. According to this hypothesis the migration velocity of a given ion at a given concentration will always be the same no matter what the other ion may be. On studying the apparent change of migration velocity with the concentration it was found that the same formula could be used for all univariant ions with the exception of hydrogen and hydroxyl. This formula may be written $l_v = l_\infty - Q\eta\lambda$, where l is the migration velocity, $\eta\lambda$ the linear concentration, and Q a constant. If the conductivities are expressed in reciprocal ohms the value of Q is 213. For hydrogen and hydroxyl as ion double to treble the normal value must be assigned to Q. In compounds containing two univalent and one bivalent ion, the change of the migration velocity of the bivalent ion with the concentration can be represented approximately by the formula for hydrogen or hydroxyl as ion. When both cation and anion are bivalent the decrease of the migration of the velocity with increasing concentration is much greater than in the case of two univalent ions. *W. D. B.*

On the electric conductivity of solutions of potassium permanganate. *E. Legrand. Comptes rendus*, **126**, *1025* (*1898*). — Conductivity determinations at 25°, 35° and 45°. The temperature coefficient for $n/16$ solutions is 0.021 between 25° and 35°, while it is only 0.014 between 35° and 45°. The author considers that his measurements at high dilutions confirm the hypothesis of Bouty that the equivalent conductivity of all neutral salts is the same at infinite dilution. *W. D. B.*

On the electrical resistance of crystallized silicon. *F. LeRoy. Comptes rendus*, **126**, *244* (*1898*). — The conductivity of crystallized silicon varies very

much with the degree of pulverization, of compression, etc. In round numbers the resistance is thirteen hundred times that of carbon and the author hopes that some day it may be used for high resistances. *W. D. B.*

On the influence of pressure on the electrical conductivity of solutions. *A. Bogojawlensky and G. Tammann. Zeit. phys. Chem.* **27,** *457* (*1898*).—When the dissociation of the solvent may be neglected, the "pressure-influence on the conductivity", $\frac{1}{\lambda}\frac{\Delta\lambda}{\Delta p}$ is expressed by $\frac{1}{v}\frac{\Delta v}{\Delta p}+\frac{1}{\eta}\cdot\frac{\Delta\eta}{\Delta p}+\frac{1}{\alpha}\frac{\Delta\alpha}{\Delta p}$ where λ = conductivity, p = pressure, v = volume, η = viscosity and α = degree of dissociation. It is first shown that for dilutions of 100 L per g-mol and upwards the first two terms of the expression may be replaced by the corresponding values for the pure solvent, which are calculated from previous data. The third term is calculated for various acetic acid and chloracetic acid solutions from the dissociation constant and volume change on dissociation. The pressure-influence on the conductivity calculated in this way for 500 atmospheres agrees satisfactorily with the experimental results. Other questions discussed are: Influence of volume change by dissociation on the pressure influence, pressure-influence in very dilute solutions (in which the conductivity of the solvent cannot be neglected) and the pressure-influence in solutions of multivalent ions. A description of the apparatus used and tables of the results obtained are appended. *F. B. K.*

Some observations of the conducting power of the burnt products of the gas flame. *K. Wesendonck. Wied. Ann.* **66,** *121* (*1898*).—The fact was first pointed out by J. J. Thomson, that air rendered electrically active, loses every trace of conducting power when allowed to bubble through water, or when passed through cotton or glass wool. Subsequent observers showed these properties of gases generally, but were rather divided as to the effect of allowing the gas to bubble through water. The author endeavors to study these points for the combustion products of the gas flame. His method is very simple and is essentially to suck the burnt products into an inverted funnel and from thence through successive vessels into a tube where it is brought in contact with the metal plate connected with an electrometer. The rate of discharge of the electrometer gives roughly the conducting power of the gas. The results of the work are to show that cotton or glass wool are equally effective in removing the conduction power and that different liquids such as water, mercury, sulfuric acid, potassium permanganate, turpentine or glycerin, contrary to the results of Townsend, produce only a slight effect when the gas is bubbled through. The greatest effect is produced by hot sulfuric acid.

The second part of the paper is devoted principally to a recapitulation of some previous results of the author's bearing on the present work. The close of the paper is devoted to an endeavor to reconcile his results with the ion theory of gases.

The whole question of the conducting power of gases, being due to minute carriers or ions, is one which seems, from the researches of J. J. Thomson and his students, to be placed beyond the region of controversy; hence it is more or less unsatisfactory to find the author going into the matter as though the question was still unsettled and undecided. *H. T. B.*

On the temperature of incandescent lamps. *P. Janet. Comptes rendus,* **126,** *734 (1898).* — When the resistance of the lamp is fifty-three one-hundredths of the resistance at 15°, the temperature is found to be 1620° while Le Chatelier found 1600° under the same conditions. *W. D. B.*

Contribution to the study of electric furnaces. *Gin and Leleux. Comptes rendus,* **126,** *236 (1898).* — Treating the arc as a resistance (See **3,** 124) the authors deduce the conclusion that if the arc were enclosed inside an adiabatic surface, the temperature of the arc would increase as the square of the current density and as the ratio of the resistance of the atmosphere round the arc to the specific heat of the enclosing atmosphere. In making calcium carbid a brilliant layer of graphite is noticed nearest the arc and farther off a layer of crystallized calcium carbid. This layer of graphite is attributed by the authors to the dissociation of calcium carbid at temperatures below the sublimation point of carbon. *W. D. B.*

Dielectricity and Optics

On the mutual action of two current circuits and the application to the determination of dielectric constants. *J. A. Erskine. Wied. Ann.* **66,** *269 (1898).* — The author brings forward a new method for the determination of dielectric constants, which depends on the attainment of complete resonance between two circuits. The current induced in the secondary circuit by a condenser discharge in the primary depends entirely on the capacity and resistance of the secondary circuit. Hence, as the author shows mathematically, by making the coefficient of mutual induction small in comparison with the coefficients of self induction, a large change in the secondary current takes place with a fairly small change in the capacity. Taking a convenient capacity for the primary and introducing a Kohlrausch condenser with adjustable plates in the secondary the way in which the current varies with the change in capacity is studied. As a very delicate current indicator the author uses the sensitive magnetic needle devised by Rutherford. Characteristic curves are given showing how the current rises rapidly as the distance between the condenser plates is diminished, passes through a maximum for the resonance point and diminishes again.

Calculating the capacity for the Kohlrausch condenser in the usual way, the capacity of any other condenser can be at once deduced by introducing it into the secondary circuit in place of the Kohlrausch condenser. The dielectric constant of a liquid of course can be calculated by measuring the capacity of a suitable condenser first with air and then with liquid. The chief source of error pointed out by the author is the introduction of substances with great absorption. The effect is to seriously change the damping of the secondary oscillations. Great care has then to be taken with the insulation. The author has evidently made a painstaking study of the method and has made careful determinations of the dielectric constants of a number of substances, but unfortunately owing to the peculiar effect produced by defective insulation, and the introduction of substances of high absorptive power in the condenser the method does not appear to hold any advantages over the ordinary methods of measuring dielectric constants. *H. T. B.*

On the conduction of electricity through thin films of dielectric substances. *W. Leick. Wied. Ann.* **66,** *1107 (1898).* — The author investigates the electric leakage effect in thin dielectric films of the order of 0.05 mm. These films of gutta percha, collodium, paraffin and sulfur are prepared between two brass plates. The resistance of the films is measured by the ordinary Wheatstone's bridge method. The most interesting results arrived at are: that the resistance of the films appears to depend on the current strength, decreasing as that increases; that the change in resistance produced by a gradual change in the current intensity shows a certain hysteresis effect; that gutta percha and paraffin show no polarization, while sulfur shows a strong polarization. *H. T. B.*

Note on the "studies on electrical vibrations" by H. Kauffmann. *E. Wiedemann and G. C. Schmidt. Zeit. phys. Chem.* **27,** *343 (1898).* — The authors call attention to their own research on this subject, Wied. Ann. **56,** 18 (1895). *F. B. K.*

On the note by E. Wiedemann and G. C. Schmidt on my studies on electrical vibrations. *H. Kauffmann. Zeit. phys. Chem.* **27,** *518 (1898).* — The author points out that there is an essential difference between his investigations and those of Wiedemann and Schmidt, in that his observations were all carried out on vapors *at atmospheric pressure.* *F. B. K.*

Studies on electrical vibrations. *H. Kauffmann. Zeit. phys. Chem.* **26,** *719 (1898).* — (*Preliminary communication*). When the vapor of a substance at atmospheric pressure is subjected to the influence of electrical vibrations induced by a Tesla current one of two phenomena is usually observed: either the vapor is traversed by colored sparks or a fluorescence of more or less brightness is produced. Only a few substances remain completely dark. Fifty-six organic substances were investigated and more or less connection between their constitution and their ability to fluoresce was noted. *F. B. K.*

On the reaction pressure of cathode rays. *E. Riecke. Wied. Ann.* **66,** *954 (1898).* — In order to determine the back pressure exerted on the electrode by cathode rays the discharge from a Töpler influence machine was sent through an electrical radiometer. From observations of the acceleration, final velocity and retardation (after short-circuiting the discharge) of the radiometer and from a determination of the moment of inertia of the vane the pressure on a unit area of the fans may be calculated. The ratio of this pressure to the current strength was found to be constant. "The reaction pressure of the cathode rays is consequently proportional to the strength of the discharge current". [Since the current varied only between 2.77 and 3.52 and the constant between 124 and 131 — almost regularly — the result is not very convincing: even assuming the pressure to vary as the logarithms of the current, as good a constant would be obtained.] In the latter part of the article the author calculates the reaction pressure from the amount of heat evolved when the rays strike the glass of the tube (Wiedemann and Ebert). Assuming that all the energy comes from the kinetic energy of the rays, he finds a pressure of the same order of magnitude as that calculated from the movement of the radiometer. *F. B. K.*

Transparency of bismuth in a magnetic field. *J. Violle. Comptes rendus.* **126,** *462 (1898).* — According to the electromagnetic theory of light there is a relation between the transparency of a substance and its electrical conductivity. Placing a thin sheet of bismuth in a magnetic field did not, however, change its transparency perceptibly. *W. D. B.*

Influence of the temperature on the rotatory power of liquids. *P. A. Guye and E. Aston. Comptes rendus,* **125,** *819 (1897).* — The following conclusions are formulated:

In general and within the limits of actual experiments the specific rotatory power of an active liquid diminishes steadily under the influence of rising temperature, without any sudden variation when the substance passes from liquid to vapor. The rotatory power of an active liquid does not appear to approach a limiting value as the temperature is raised more and more.

An exception to these conclusions is to be found in amyl alcohol. Here the specific rotatory power first decreases and then increases with rising temperature. This can easily be accounted for by assuming that the polymerized liquid alcohol has a lower rotatory power than the unpolymerized alcohol. At low temperatures where the change in the polymerization is slight, normal results are obtained. With further rise of temperature the change due to the depolymerization is an important one. The following facts may be cited in behalf of this hypothesis. According to Ramsay and Shields liquid amyl alcohol is strongly polymerized. In aqueous solutions the specific rotatory power is very nearly that of pure vapor, while in benzene solution the specific rotatory power is less than that of the pure liquid. *W. D. B.*

On the rotatory power of polymeric substances as compared with those of their monomers. *M. Berthelot. Comptes rendus,* **125,** *822 (1896).* — Referring to the results of Guye and Aston (preceding review) the author recalls the facts, observed by him, that the rotatory power of metaturpentine is less than that of isoturpentine and that the rotatory power of styrene is less than that of metastyrene. *W. D. B.*

On the rotation dispersion of tartaric acid and of turpentine. *G. V. Wendell. Wied. Ann.* **66,** *1149 (1898).* — The author makes a few additions to the facts and theories of this subject — the latter being more striking than the former; "To me it appears that the gradual alteration of the relative distances of the atoms, their arrangement and their movements with increasing dilution must have a very marked effect on the elasticity and density of the ether and that they consequently exert a much greater influence on the rotation than is usually supposed". *F. B. K.*

On the spectrum of carbon in fused salts. *A. de Gramont. Comptes rendus,* **125,** *172, 238 (1897).* — By regulating the potential difference of the discharge the author has succeeded in obtaining the spectrum of carbon from fused salts and from graphite. With the fused salts only the lines of carbon were seen; but with Siberian graphite from the Alibert mine the band spectrum of Swan was also obtained. *W. D B.*

Note on the spectra of hydrogen. *T. W. Richards. Am. Chem Jour.* **21,** *172 (1899).* — The 'red' spectrum of hydrogen can be obtained more readily with water vapor than with hydrogen, the reason apparently being that the water can be dissociated into ions at a lower temperature than can hydrogen. The author agrees with Hasselberg and with Hutton in believing that the so-called 'cool' white spectrum of hydrogen is not due to impurities. He also points out that Randall's results are really in harmony with those of Trowbridge and Richards. (See **1,** 457; **2,** 60). *W. D. B.*

On the spectrum and nature of neodidymium. *E. Demarçay. Comptes rendus,* **126,** *1039 (1898).* — Starting from the double ammonium nitrate the author has obtained pure neodidymium, the purity being determined both by the spectroscope and the colorimeter. The pure oxid is a clear blue with lilac tints in the shadows. The salts vary from a lilac blue to a reddish violet, depending on the thickness. Traces of samarium or praseodidymium change the color of the oxid and of the salts very markedly. *W. D. B.*

On the electromagnetic rotation of the plane of polarization in salt solutions. *S. Oppenheimer. Zeit. phys. Chem.* **27,** *447 (1898).* — Careful determinations of the electromagnetic rotation of solutions of sodium chlorid, potassium chlorid, sodium bromid, potassium bromid, cadmium chlorid and acetic acid show that the specific rotation for these substances is independent of the concentration. *F. B. K.*

Rays emitted by compounds of uranium and of thorium. *S. Curie. Comptes rendus,* **126,** *1101 (1898).* — The rays from compounds of thorium are more effective in increasing the conductivity of the surrounding air than are the rays from the compounds of uranium. Curiously enough, natural chalcolite is much more active than artificial chalcolite and the author therefore suspects the existence of some active metal in the mineral. Although white phosphorus is very active, the fact that red phosphorus and the phosphates are inactive makes it probable that the cause of this activity is not the same as in the case of uranium and thorium. *W. D. B.*

On the light absorption of uranyl salts. *E. Duessen. Wied. Ann.* **66,** *1128 (1898).* — A detailed investigation of the absorption spectra of various uranyl salts in water, alcohol, glycerin, ether, ethyl acetate, methyl alcohol and acetone. In order to identify the corresponding lines in the different solvents the displacement was followed where necessary, through intermediate mixtures. Photometric measurements both of the total absorption and of the individual lines were also carried out. No general conclusions of importance were arrived at. *F. B. K.*

On the relation between the color and the constitution of the halid double salts. *N. S. Kurnakow. Zeit. anorg. Chem.* **17,** *207 (1898).* — An attempt to show that in the double chloroplatinates crystallizing with ammonia the color of the solid salt depends on whether the ammonia belongs with the $PtCl_2$ or with the other chlorid. Incidentally, several salts are discussed which undoubtedly form solid solutions with water, though this point is not recognized by the author. *W. D. B.*

An illumination apparatus for monochromatic light with fixed slits. *R. Straubel. Wied. Ann.* **66,** *350 (1898).* — The author merely describes the application of a prism with variable angles to a spectroscope so as to minimize the numerous adjustments necessary when monochromatic light is used. The construction and position on the spectroscope are briefly described.

H. T. B.

Crystallography, Capillarity and Viscosity

On the crystallographic identity of the dextro-rotary and laevo-rotary asparagins. *P. Freundler. Comptes rendus,* **125,** *657 (1897).* — According to the measurements of Grattarola the crystals of dextro-rotary asparagin differ slightly from those of laevo-rotary asparagin, and this has been cited by Walden (**1,** 460) as an exception to Pasteur's law of hemihedral forms. The experiments of the author show that this discrepancy does not exist. *W. D. B.*

A study of the surface tension of water in narrow capillary tubes. *P. Volkmann. Wied. Ann.* **66,** *194 (1898).* — This paper is the outcome of the discussion between the author and Quincke (**2,** 76) on the merits of their respective methods of measuring the surface-tension of water. The method of Quincke embodied the use of narrow dry tubes of 0.2 to 0.1 mm diameter, while that of the author wet tubes of larger bore, 0.5 mm. In order to explain the difference between the author's results and those of Quincke he undertakes a careful series of experiments to determine to what extent the capillary height depends on the composition and character of the glass and to what extent it varies with the area of the tube. He uses six different kinds of glass of different composition, both hard and soft. His method of procedure was to draw the capil lary from pieces 1 cm in diameter. Closing off the tube without allowing the gas flame to come in contact with the interior, he immerses the fused end in water and breaks it off. The capillary height is read by means of a cathetometer reading to 1/100 mm. He finds this a much quicker way than with the long micrometer screw and observing telescope, employed in his previous work. The capillary tubes are placed in a water-bath together and the cathetometer about 30 cm away.

The results of the work show that capillary constant is unaffected by the composition of the glass, within the limit of his measurements, 0.01 mm^2, and that for the narrow tubes of from 0.1 to 0.3 mm the capillary constant was 0.044 mm^2 and the surface-tension 0.022 mg/mm greater than for his older observations with larger tubes. No difference could be found using moist or dry tubes. The author claims the differences found by Quincke for fresh drawn or old tubes were probably due to errors in the determination of the areas of the tubes he used. The author rightly emphasizes the importance of careful measurements of the area of the tubes and marks a fine line in order always to bring the water level to a known part of the tube. This he claims Quincke neglected to do.

H. T. B.

On the surface tension of mercury. *J. Stöckle. Wied. Ann.* **66,** *499 (1898).* —A summary, made by Quincke, of the surface-tension of mercury has shown that this varies between wide limits. The author considers this not due alone to

errors of observation but much more to the well known continuous decrease noted in making determinations of the surface-tension of mercury. The present paper is a record of a very careful series of observations made by the author in order to find out in just what way and to what extent the surface-tension varies. The method is that of Helmholtz and König and consists in measuring the size and curvature of mercury drops. Instead of using the approximate formula of Poisson for the determination of the surface-tension, which was shown by Lohnstein to be merely a very rough approximation, the author uses the method of Bashforth and Adams i. e. determining the capillary surface by mechanical quadrature. The author gives a very clear description of the apparatus used.

The results of the work show that the surface-tension is constant both in vacuum and mercury vapor and amounts to 44.3 mg/mm. The tension is greater on fresh surfaces of mercury in gases, but gradually decreases, finally approaching the value in vacuum. The decrease takes place rapidly in hydrogen, and slowly in nitrogen. This decrease in value is to be ascribed to a condensation of the gas on the mercury surface and not to the accumulation of fatty vapors. (Compare next review.) *H. T. B.*

The surface tension of mercury in gases. *G. Meyer. Wied. Ann.* **66**, *523 (1898).* — The results obtained by Stöckle (see last review) show that the surface-tension of mercury in the presence of gases is much greater than in vacuum. In order to further prove this point the author studies the surface-tension of mercury flowing from an elliptical orifice into the gas. This of course offers continuously a fresh surface and prevents the falling off in surface-tension, characteristic of the statical method. The method consists in measuring the wave length set up in the mercury column flowing both in gas and in vacuum. If λ represent this and p the pressure under which the mercury flows into the vacuum, then T the surface-tension is represented by the relation

$$\lambda = \text{const} \sqrt{\frac{p}{T}} .$$

In a gas the values λ, p, and T, are simply substituted. Hence knowing T, the surface-tension in vacuum, the values can be deduced from different gases.

The author compares his results with those of Stöckle's accepting the latter's value of the surface-tension in vacuum. The results are all higher and show undoubtedly the enormous effect produced by the gases.

Gas	Meyer dynamic method	Stöckle static method
Air	51.5	48.8
O	51.4	48.7
N	50.5	49.8
CO_2	49.6	49.0
H	56.5	47.9

The author discusses the possibilities of error in the method of Quincke, which in air gives such a large value i. e. 55.8 mg/mm. No satisfactory conclusions are, however, arrived at. *H. T. B.*

THE COMPOSITION OF MIXED VAPORS, I

BY HECTOR R. CARVETH

It has long been known that only in the cases of a chemical compound absolutely pure, and of a few two-component systems which show a maximum or minimum vapor-pressure is the percentage composition of the vapor phase the same as that of the liquid phase with which it is in equilibrium. From the slight knowledge of this subject has been deduced the theory of fractional distillation to cover the cases where both components are volatile, that is when their boiling-points do not lie too far apart. When, however, as in the case of a salt and water, there is a great range of temperature between the boiling-points, the assumption is made that the component with the higher boiling-point is non-volatile, and on this rests the present day theory of the rise of the boiling-point in dilute solutions. Of course there can be no absolute division of chemical bodies into volatile and non-volatile classes; everything depends on the conditions of the experiment. Any theory, therefore, which is based on the relative non-volatility of one of the components cannot be of general service. It is unfortunate that the majority of physical chemists appears to be satisfied with the theory which applies not to the general, but to the particular case, and even then for very dilute solutions only—and leave out of the range of their research the examination of dilute solutions where both components are volatile.

This may therefore be given as one reason why it is that the experimental side of the determination of vapor compositions has been so poorly developed; but this cannot explain why the organic chemist has failed to use the best methods in examining the possibilities of separation of the components in mixtures. The truth of this statement is supported by the paucity of the

cases given in chemical literature where there has been determined with *any* degree of accuracy the compositions of liquid and vapor phases which are in equilibrium at any pressure whatever, while the cases exemplifying separations carried out under the ordinary conditions of laboratory or actual technical work have (so far as the writer is aware) not been attacked at all. The scope of the field is hence very great.

Another reason, and one perhaps more important, is that such determinations have hitherto been made only with great trouble. All methods which have been employed have required that the vapor shall be removed from above the solution, condensed, and then analyzed by titration,[1] surface tension,[2] optical[2] or density[3] methods or by ultimate chemical analysis.[4] The objection which must be raised to every method of vapor composition determination is that, since the composition of the vapor is different from that of the solution, its continuous removal for the purpose of analysis changes the composition of the solution with which it was in equilibrium. An instance of the extent of this change will be shown later in the discussion of the results obtained by Brown.[3]

The method whose description and illustration is the especial object of this paper rests to a certain extent under the same disadvantage as all previous ones, but it is believed that easily determined corrections may be introduced which will render it exact in its determination of vapor composition; and although laboratory experience is disclosing some imperfections in the apparatus used, it has been thought advisable to publish the method and the few results obtained by its use up to the present.

Expressed very briefly the new method suggested is this: The condensed vapor is returned to a small receiver within the larger flask containing the solution whose boiling-point is being taken (pressure constant), and in this receiver the condensed

[1] Duclaux. Ann. Chim. Phys. (5) **14**, 305 (1878).
[2] Lehfeldt. Phil. Mag. [5] **40**, 398 (1895); **46**, 42 (1898).
[3] Brown. Jour. Chem. Soc. **35**, 547 (1879); **39**, 304 (1881).
[4] Linebarger. Jour. Am. Chem. Soc. **17**, 617 (1895).

vapor is made to boil. From this boiling-point one may, by consulting the boiling-point curve of the two liquids, determine with a very fair degree of accuracy the composition of the condensed vapor.

It is thus apparent that first of all there must be found the boiling-point curve for the two liquids. The compounds which were first used in this work were acetone and water, and as no complete data could be found from which the curve for these substances could be constructed, it was necessary first of all to determine the curve by experiment.

The boiling-point of pure acetone was taken, making use of the Beckmann apparatus and then weighed amounts of water were added and the corresponding boiling-points noted. Then, the same apparatus being used, the boiling-point of water was noted, small amounts of acetone added and readings taken. Here, however, practical difficulties made it necessary to discard the Beckmann apparatus as unsuited for this work.

As the vapor in equilibrium with dilute aqueous solutions of acetone contains a far larger percentage of acetone than does the solution, it is necessary, if one wishes to obtain a constant thermometer reading at constant pressure, that the heating must be performed very uniformly — or in other words, when this Beckmann apparatus was used, it was found possible to raise or lower the boiling-point and *keep it fairly constant at one point* by changing the rapidity of the heating. (The possibility of radiation from the source of heat was of course excluded by the use of asbestos mantles.) The larger the condensing chamber the greater were the variations observed. Moreover it was found that when the tube containing the condensed vapor dipped *below* the surface of the liquid in the boiling-flask (as is invariably shown in text-books on physicochemical methods) small explosions occurred which were due to the sudden superheating of the returned condensed vapor. This is easily understood when it is stated that in this especial case the condensed vapor frequently has a boiling-point lying twenty-five degrees below that of the solution with which it had been in equilibrium, and consequently

it must have a very high vapor-pressure at the temperature of the boiling solution. The Beckmann apparatus cannot therefore be used with two components which are both sensibly volatile unless special precautions are taken.

It was then decided that the most accurate readings could be made only by making use of large amounts of solution with a relative small vapor space above for the condensing chamber.

The boiling-point readings therefore were taken after adding small amounts of acetone to water in a one liter balloon flask, the condensing chamber being a long Liebig condenser. The amount of solution used was never less than 400 cc. The acetone was added through the condenser after the solution had been allowed to cool down sufficiently. Diffusion of the vapor into the air was practically prevented by the very cold surface of the condenser walls, and by having a cork fitting loosely in the top. Making use of this simple apparatus, it was very easy to obtain readings constant to tenths of degrees, whereas with the Beckmann apparatus it was not at all unusual to have readings vary whole degrees by mere variation of the rate of heating.

When the whole boiling-point curve had been determined, a third hole was made in the cork of the liter flask and through it was passed a glass tube AB, blown as shown in the figure (see Fig. 1). Its length was 18 cm, mean diameter 20 mm, capacity of bulb B up to the side opening D about 8 cc. Through the drawn-out portion of the bulb B is sealed a rather heavy platinum wire G, whose purpose is to help conduct heat from the boiling solution outside to the contents of the receiver B. In the sides of the latter are two openings D and E, the former allowing the vapor and excess of condensed vapor to return to the boiling solution, while through the latter (E) passes the glass tube which serves to catch the condensed vapor, and deliver it through a small opening at the end of the tube into the receiver B, just above the platinum wire. Above the lower end of this tube and just above G are placed, in such amount as practically to fill the bulb B, tetrahedra made either of silver, copper or platinum. Any of these, it may be remarked, are infinitely bet-

ter as a means of conveying heat than the beads, agates, etc., which are so frequently used in boiling-point determinations.[1] The thermometer which is placed in the tube AB is always in-

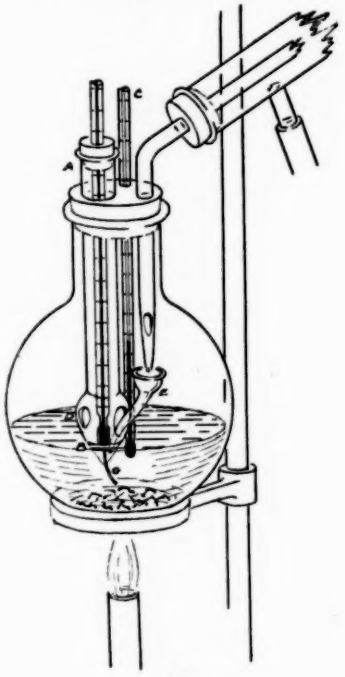


Fig. 1

serted to such an extent that no part of its bulb is as high up as the opening D.

Starting now with any solution of the two components, acetone and water, one arranges the apparatus so that one thermometer is in the solution, and the tube AB is so placed that no liquid can enter it at D and no condensed vapor can fall from the return condenser into E. The solution is heated and the boiling-point noted. When several readings have shown this to be con-

[1] Compare Beckmann. Zeit. phys. Chem. **21**, 248 (1896).

stant, the whole tube AB is turned so that the liquid from the condensing tube may keep dropping into E, and then AB is slowly lowered into the solution. The extent of this lowering must depend on different circumstances. Thus, in case there is a great difference in the boiling-points of the vapor and solution, it will often be found necessary to let only the platinum wire G come into contact with the solution in the larger flask. In case there is no great difference in the boiling-points, it may be necessary to immerse the bulb B to a considerable extent, but *never* up to the opening D. Under these circumstances the liquid in B will boil vigorously, provided that one avoids superheating by having sufficient of the tetrahedra present, and that one does not allow all of the condensed vapor to pass into the receiver B. No fixed rule can be laid down to regulate these details, a knowledge of which is acquired after a very short practice. The writer has found, however, that superheating is apt to cause more trouble than having an excess of the condensed vapor return, since the latter can be so readily checked by narrowing the receiving tube at its point of delivery above G.

When the liquid in the receiver starts to boil, it will be noticed that the reading of the thermometer immersed in it shows lower and lower temperatures, until finally it becomes constant, rarely varying 0.05° in an hour. This constant reading gives the boiling-temperature of the condensed vapor, whose composition may now be very readily determined from the boiling-point curve.

When a series of readings are to be made, the modus operandi is varied but slightly. First of all one determines whether one of the pure components gives a vapor whose boiling-point is the same as that of the component. If the liquid be absolutely pure this must be the case. If it is not, there may be a slight variation. With the apparatus described in this paper, it has not been found possible to have the returned vapor in the inner tube boil vigorously unless there was a difference of about one degree in the boiling-points of the two liquids. The heat supplied from the outer liquid must be sufficient to heat up the returned

vapor to its boiling-point and vaporize some of it. The conduction of the heat must therefore be very rapid if the condensed vapor is returned rapidly, and it is very doubtful therefore if glass is the best material for the construction of the bulb B when dilute solutions are being used. Experiments are being made with a silver receiver to ascertain if it is not possible to have vigorous ebullition in the inner tube when there is but a very slight difference in the boiling-points of liquid and vapor. Such a result can undoubtedly be obtained by varying the size of the apparatus and introducing electric heating of the inner tube, but it is hoped that a more simple form of apparatus may prove satisfactory. With such a device one could ascertain the purity of a substance by the boiling-point method very quickly. The advantage of this over the ordinary method would be that variations of pressure during the operation could be completely ignored.

After the preliminary determination, the other component is added in small known amounts, the tube AB is lowered until both openings E and D are below the level of the solution, and the flask is heated until the readings of both thermometers show the same temperature — the boiling-point of the solution. The receiver AB is now raised and turned to catch the returned condensed vapor. This will in time completely displace the solution with which it has been filled, and soon show a constant boiling-point. One must now note also the temperature of the boiling liquid outside. It will sometimes show a rise of 0.05° to 0.10°. It is from the extent of this rise that corrections, if required, must be calculated. After these boiling-points have been determined, the bulb is again totally immersed in the solution when both thermometers must again show the original readings. It will be seen that, by working in this manner, a continuous series of readings may be made quickly, the boiling-curve of the solutions and that of the vapor being determined at the same time. This is the method which was used in the case of benzene and carbon bisulfide and is decidedly more expeditious than the one previously described for the case of acetone

and water, where the boiling-point curves are determined separately.

The very important question in connection with this work which presented itself at the outset was "Does the presence of the great volume of solution boiling at a far higher temperature influence the reading of the thermometer in the tube AB?" If this does have any effect, it will render the method useless in so far as its claim as a method of analysis is concerned. But continued observations showed that, when the liquid in the bulb was boiling regularly, neither immersion almost to the opening D nor raising until the point G just touched the surface of the liquid, caused an appreciable (i. e. up to 0.02°) variation in the reading. This cannot be said of the preliminary measurements, as the writer had then to overcome the difficulties due to superheating, crude form of apparatus, etc. The inner boiling-tube described in this paper has been selected only after experiments had been tried with scores of others of different sizes and shapes. The constancy of the readings as finally obtained from the apparatus in its present form forces one to the conclusion that the ebullition of the liquid around the thermometer in B cuts off all heat effects due to the proximity of the outer solution, and that this thermometer can indicate a temperature none other than that of the liquid boiling in the bulb B.

The temperature measurements were made with two 100° thermometers divided into tenths of degrees. These were carefully compared with a Reichsanstalt, and all readings given are corrected. The pressures as given in the first two tables are not corrected, since the corrections as applied would be small in proportion to other errors present in the method in its first application. In the tables V, VI, and VII the pressures given are corrected.

The first table contains the data for the boiling-point curve for acetone and water. Column I shows the percentage in grams of acetone in the solution, Column II the boiling-point of this solution, Column III the barometric pressure at the time the boiling-point was taken. The determinations were not all made on the same day.

TABLE I

I % Acetone	II B Pt	III Bar	I % Acetone	II B Pt	III Bar
100.0	56.15°	748.4	23.61	68.95	736.6
95.29	57.22	748.4	18.90	71.90	740.0
89.19	58.33	748.2	17.21	73.31	740.3
84.65	58.99	738.9			
77.79	59.74	748.6	16.49	73.56	739.5
72.07	60.45	748.6	12.46	77.16	740.0
65.86	61.02	748.7	9.58	80.70	739.6
54.74	62.08	748.4	4.56	88.70	739.5
46.71	63.23	741.8	1.9	94.63	740.1
35.90	65.91	741.6	0.0	99.26	740.2

The next table shows the boiling-points of the condensed vapors as compared with those of the solutions with which they are in equilibrium. At once the question arises: — how do the determinations made in this manner compare with those found by other methods? In answering this, the writer made use of the still-head method proposed by Brown[1] in order to obtain and analyze the vapor given off by a solution at a given temperature.

The method rests on the principle that the composition of a vapor issuing freely from an opening depends on the temperature of the surrounding walls. If the temperature be higher than that at which the substance vaporizes, the vapor will pass on unchanged in composition. If the temperature be lower than that of the vapor passing into the worm of the still-head, condensation either total or partial will take place, and whatever vapor escapes from the top of the coil will have the same composition as if it had been removed directly from a solution boiling at that temperature. The temperature of the vapor in the still-head and not the boiling-temperature of the solution in the still-head determines therefore the composition of the issuing vapor, so long as the still-head temperature is not higher than that of the boiling solution.

The advantage of using this method should lie in the fact that the only precautions necessary in its use are that all the vapor should be condensed after its removal from the worm, and

[1] Brown. Jour. Chem. Soc. **39**, 517 (1881).

that the temperature of the issuing vapor should be constant. In the measurements recorded below, these details have been properly attended to.

In this table of comparison (Table II), the first column shows the boiling-point of the acetone in the outer flask, or the temperature of the still-head (these latter measurements being marked with an asterisk); the second column shows the boiling-point of the condensed vapor in the tube B, or the boiling-point of the distillate from the still-head (also marked with an asterisk); the third column the pressures, which are not corrected.

TABLE II

I B Pt solution	II B Pt vapor	III Bar	I B Pt solution	II B Pt vapor	III Bar
62.45°	57.4°	745	82.1°	60.2°	736
63.6	57.9	745	82.55	60.35	735
*65.5	*57.4	733	82.60	60.28	735
65.75	58.0	741	84.15	60.52	735
*67.0	*57.75	733	85.0	60.6	735
68.3	58.6	740	88.0	61.43	735
*69.0	*58.4	733	*90.0	*61.90	732
70.85	59.0	741	90.4	62.0	734
71.9	59.15	740	*91.4	*63.60	728
*73.0	*59.2	734	92.0	64.55	734
73.8	59.25	738	94.1	65.05	735
75.8	59.48	738	*94.0	*65.90	728
77.15	59.7	737	94.5	66.90	735
78.9	59.95	737	95.3	68.3	735
*80.5	*59.8	731			

The data of Tables I and II are represented graphically in Fig. 2,[1] the curves being plotted in the ordinary manner. For example a solution of boiling-point X returns to the bulb B a liquid whose boiling-point lies at Y. The point Z on the vapor composition curve is thus determined.

The results obtained by the different methods agree quite well, but in almost all cases the still-head method shows more acetone present in the distillate than is found by the other method, the maximum difference being slightly over one per-

[1] It is probable that the waviness in the lower end of the curve does not represent the facts as a smooth curve would have done.

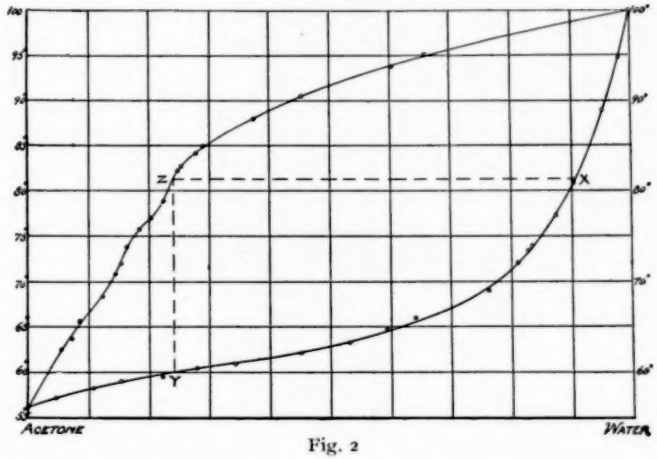


Fig. 2

cent. The uniform variation in the one direction may be explained in one of two ways:

(1) In the returned-vapor method, it is possible that the vapor, descending, is deprived of some of its more volatile component before it reaches the tube B, and if this proceeds uniformly the boiling-point will be constant, and give a higher reading than it should.

(2) In the constant still-head method as used by the writer, some error is present which allows more of the more volatile component to pass over than corresponds to the true composition of the vapor.

Owing to the small differences observed in the results from the two methods when acetone and water were used, it was thought advisable to further test the method by a case which had been examined by another investigator,[1] where preliminary measurements showed the probability of considerable difference. The components were benzene and carbon bisulfide. Considerable care was taken to obtain these substances pure. The benzene was first fractionated, then shaken repeatedly with concentrated sulfuric acid, crystallized out and again subjected to

[1] Brown. Jour. Chem. Soc. **35**, 547 (1879).

fractional distillation. The carbon bisulfide was shaken with sulfuric acid, mercurous sulfate, then with mercury and finally fractionated over lime.

The results obtained by our own apparatus are given in Table III. In columns I and II are given the percentages (always in grams) of the carbon bisulfide and benzene which correspond to the boiling-points given in column III, the barometric pressure being shown in column IV. In the last column are given the boiling-points of the condensed vapors corresponding to the respective solutions.

TABLE III

I % Acetone	II % Benzene	III B Pt solution	IV Bar	V B Pt vapor
0.00	100.00	79.58	738.8	79.54
3.04	96.96	77.07	737.9	73.70
8.61	91.39	73.48	737.4	66.65
18.11	81.89	68.17	739.3	60.25
25.74	74.26	64.56	739.3	56.80
31.88	68.12	62.02	739.3	54.38
40.45	59.55	58.90	739.4	62.30
49.66	50.34	56.32	742.4	51.35
55.21	44.79	54.70	742.4	50.45
58.56	41.44	53.85	742.5	50.10
64.57	35.43	52.40	742.5	49.20
73.01	26.99	50.70	742.6	48.25
79.47	20.53	49.38	742.6	47.75
87.29	12.71	47.93	744.0	47.00
100.00	0.00	45.82	744.1	45.75

When the data obtained above are plotted and compared with the results given by Brown[1] in his final table, it is found that they do not agree. The reason is not far to seek. Brown determined his boiling-point curve, not by measurement of the boiling-temperature of solutions of known concentration, but from the composition of the vapor he calculated the composition of the solution remaining in the flask, and gave this boiling-point as being for this concentration. Any error in the vapor analysis would at once show itself in the boiling-point curve. If his

[1] Brown. Ibid, **35**, 561 (1879).

method were perfectly reliable, if at any time he could determine accurately the composition and amount of the vapor condensed, his boiling-points should be perfectly accurate and agree with each other. That this is the case cannot be said.

In the following table there are collected the data given in Brown's tables numbered II, V, VIII, XI, XII and XVII, no essential ones being omitted. In the first column is given the molecular percentage of carbon bisulfide in the solution, this being determined as above stated. In the second column is given the boiling-point corresponding to this composition. The first measurement in each table represents the first distillation performed.

TABLE IV

% CS_2	B Pt	% CS_2	B Pt	% CS_2	B Pt
Table II $p = 772$		Table V $p = 763$		Table VIII $p = 757$	
....	....	....	....	70.86	51.00
61.95	52.5	61.76	52.0	61.81	52.90
44.80	58.0	44.50	58.0	Table XI $p = 750$	
....	....	....	....	40.8	56.0
38.60	60.0	38.80	60.0	38.64	59.0
25.86	66.0	25.81	66.0	25.91	63.8
....	....	....	....	Table XIV $p = 752$	
19.59	70.0	18.96	70.0	18.33	66.2
....	....	Table XVII		....	....
....	....	9.44	70.6	9.69	72.4

Solutions having the compositions of 61.8 percent carbon bisulfide have given as their respective boiling-points, 52.5°, 52.0° and 52.9°; with 38.6 percent of carbon bisulfide, the boiling-points are 60.0°, 60.0° and 59.0°; with 25.8 percent, 66.0°, 66.0° and 63.8°; with 19 percent approximately, these boiling-points are 70.0°, 70.0° and 66.2°; with 9.44 and 9.69 percent the boiling-points are 70.6° and 72.4°. With the single exception of the first case, it will be noted that the boiling-point of a solution made up in definite amounts is lower than that which would be calculated from the composition of the vapor. This must mean that the method which was used kept taking away a greater percentage of the more volatile component than actually exists in the vapor.

With the view of still further testing the agreement of the results obtained by distillation, the writer has rearranged those of Brown's tables which are numbered I, IV, VII, X, XIV, and XVI. In the first column of Table V will be found the mean boiling-point at which distillation was effected; in the second is given the vapor composition expressed in molecular percentage of carbon bisulfide. From the mean boiling-points it is impos-

TABLE V

I Mean B Pt	II Vapor composition	I Mean B Pt	II Vapor composition	I Mean B Pt	II Vapor composition
Table I		Table IV		Table VII	
....	....	....	....	51.1	88.27
53.25	82.94	53.00	84.26	53.10	83.37
54.50	81.24	54.50	82.45	....	....
57.00	75.36	57.25	76.24	Table X	
59.00	70.26	59.00	72.48	59.3	68.35
61.50	64.05	61.50	66.67	61.4	63.21
64.50	56.44	64.50	59.14	64.3	55.46
....	....	....	....	Table XVII	
....	....	....	....	67.2	47.88
68.00	45.76	68.00	49.56	68.57	43.55
....	....	....	....	71.75	33.47
....	....	....	....	Table XVI	
....	....	....	....	71.6	29.50
72.50	30.56	72.50	33.85	73.2	24.36
76.50	15.05	76.92	16.27	76.45	11.80

sible by a consideration of this table to ascribe to the determination of the vapor composition any great accuracy. Variations are present ranging from one-half to nine percent so that it is absolutely impossible to use the data obtained by Brown in proof of a thermodynamic formula.[1]

From the consideration of Table IV it follows that the curve showing vapor compositions (Brown's results) is displaced toward the side of the more volatile component, and since it is in this direction that this curve departs from the one constructed from the data given in Table III, it is necessary to find where the error is present.

[1] Compare Lehfeldt. Phil. Mag. [5] **40**, 398 (1895).

The sources of probable error have been mentioned in the consideration of the discrepancies in the determinations for acetone and water. Of these the first one which will be considered is that due to the still-head. Very careful experiments were now made to see if any other precaution in obtaining a distillate of constant composition were necessary beside that of maintaining a constant temperature in the still-head itself. It was found that the writer had overlooked possible condensation in the adapter which connects the still to the worm of the still-head. In the acetone-water distillation by the still-head method this adapter was very short, and of considerable diameter and was surrounded by asbestos. In the benzene carbon bisulfide distillation, an adapter fifteen centimeters long was used, and it also was covered by asbestos. Nevertheless condensation occurred in it, and this rendered the method useless as a method of comparison.

Since the results obtained by Brown when he used the still-head agreed with those he had previously determined by direct distillation, and since it has been demonstrated in Tables IV and V that these results do not agree very well with each other, it is necessary to obtain results by some other method if a just comparison is to be made. Moreover there is the possibility that the benzene used by Brown may have contained thiophene, whose effect cannot be stated.

For this purpose a one litre balloon flask was fitted with a cork through which passed a thermometer and a tube leading to a Liebig condenser. The neck of this tube was heated up to and beyond the bend by an electric coil, which was again surrounded by asbestos. This prevents all condensation of the vapor before it passes into the condensing tube. From this condenser it flows into a receiver which holds about 35 cc and from which it could be drawn off by means of a stop-cock. This receiver has attached to it a glass arm which allows of communication with the air outside by means of a small opening at the side. In this way one is sure that if the distillation be carried on moderately, the condensation should be almost perfect, but it is very doubtful if complete condensation were

attained. The observations necessary are initial and final boiling-points of the solution which is being distilled, boiling-point of the distillate and the corresponding barometric pressures.

In Table VI are given the results obtained with carbon bisulfide and benzene; in column I the initial and final boiling-points, in II the mean of these readings. Column III contains the boiling-point of the distillate, and IV the corresponding pressures.

TABLE VI

I Boiling-points Initial	Final	II Mean B Pt	III B Pt vapor	IV Bar	I Boiling-points Initial	Final	II Mean B Pt	III B Pt vapor	IV Bar
48.1	48.5	48.3	47.25	737.9	64.1	64.9	64.5	55.85	751.8
48.5	49.0	48.75	47.30	736.8	64.9	65.7	65.3	56.55	751.7
49.0	50.1	49.55	47.55	736.3	65.7	66.5	66.1	57.50	751.7
50.1	50.7	50.4	48.00	732.0	66.5	67.6	67.05	58.10	751.7
51.1	51.8	51.45	48.30	735.5	67.6	68.6	68.1	59.35	751.5
51.8	52.6	52.2	48.96	735.1	68.7	69.8	69.25	59.31	743.8
52.6	53.7	53.15	49.42	735.6	69.8	71.0	70.4	60.52	743.7
53.7	55.6	54.65	49.80	735.7	71.0	72.2	71.6	62.75	743.5
55.6	58.5	57.05	50.80	735.8	72.2	73.5	72.85	64.62	743.4
58.8	59.1	58.85	52.05	751.6	73.8	75.0	74.4	66.71	743.2
59.1	59.6	59.35	52.65	751.6	73.0	75.9	75.45	68.58	743.0
59.6	60.1	59.85	53.04	751.5	76.3	77.0	76.35	71.60	742.8
60.1	60.9	60.5	53.41	751.4	77.0	77.8	77.4	74.58	742.6
60.9	61.7	61.3	53.55	751.4	77.8	78.4	78.1	75.55	742.5
61.7	62.6	62.15	54.08	751.4	78.4	78.9	78.65	77.42	742.3
62.6	63.4	63.0	54.62	751.5					

When the results given in the table are plotted and compared with those of Table III, it is seen that the two methods do not give concordant results. If one assumes that the distillation method used in the comparison gives results which are approximately correct — which assumption appears very reasonable — it is certain that the other method is not accurate. But the variations are again in the same direction as before — the boiling-points of the vapor as determined by this especial apparatus are all of them too high. As it has been shown previously that this could not be due to radiation, it must mean that not all of the more volatile component is returned to the tube B. If the condensed vapor flowing back into the flask comes into contact

with the ascending vapor of which the temperature is considerably higher, it seems not unreasonable to suppose that the ascending vapor might take along with it from this liquid some of the more volatile component so that the liquid which actually drops into the bulb B has not the actual composition of the vapor. Moreover it seems not impossible that, if the heating be performed regularly, the boiling-point of this returned liquid might remain perfectly constant.

In order to examine this possibility the writer has altered the form of the condensing tube. In place of having the vapor sweep continuously along a considerable length of the condensing tube which is wetted by the returning liquid, the vapor enters this tube through a hole near the cork. The actual condensation takes place as close as possible to the flask which contains the boiling solution. The returning vapor drops to the lower part of the condensing tube which is drawn out to a point, and from this it falls into the bulb B. In Fig. 1 is shown the apparatus in the form finally used.

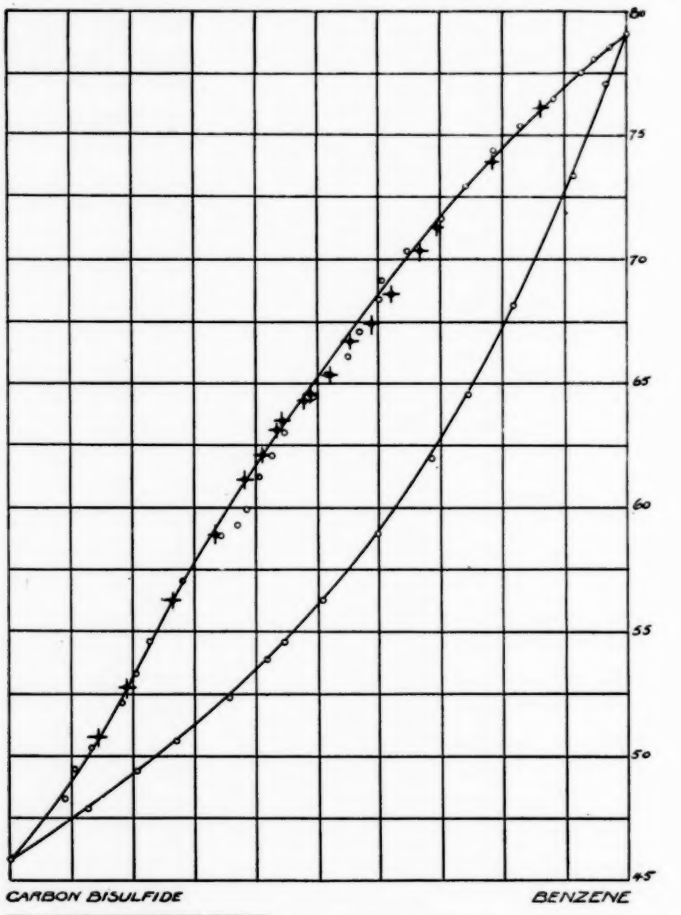
The following table gives in column I the boiling-point of the solution in the outer flask; in column II the corresponding boiling-point of the condensed vapor in tube B; in column III the pressures at which these measurements were taken.

TABLE VII

I B Pt solution	II B Pt vapor	III Bar	I B Pt solution	II B Pt vapor	III Bar
50.70	48.25	739.5	64.80	56.14	739.6
52.46	49.04	739.4	65.38	56.74	739.7
56.15	50.52	739.4	66.60	57.75	739.7
58.91	52.01	739.4	66.70	57.80	739.6
61.20	52.82	730.2	67.33	58.68	739.6
62.28	53.91	729.8	68.58	59.81	739.6
63.19	54.26	729.4	70.30	61.28	739.5
63.48	54.70	729.1	71.30	62.55	739.4
64.02	55.48	739.7	73.90	66.51	739.4
64.24	55.68	739.7	76.00	70.52	739.3
64.30	55.76	739.7			

When the results given in Table VII are plotted and compared with those given by the distillation method (Table VI) it

will be found that the curves of vapor composition coincide very well. In Fig. 3[1] the determinations given in Table VI are represented by a dot, while those of Table VII are represented by a cross. The variations of the former from the probable curve



[1] No attempt has been made to correct for the varying pressures, so that the curves are really only approximations.

seem to be greater than those of the latter, and are undoubtedly due to the loss of carbon bisulfide in the distillation, although considerable care was taken to avoid this almost certain source of error by keeping the condenser at about 3°. Moreover, the fact that the boiling-points as determined by the returned-vapor method lie *lower* than those found by the distillation method gives a strong support to this conclusion.

The fair agreement between the results as given by the two different methods shows that at least one source of error in the original apparatus has been detected and almost entirely overcome. While it is apparent that *absolute* accuracy (in this instance the error is probably not greater than ± 1 percent) may hardly be attained owing to the action of the ascending vapors on the descending liquid, still the results prove the method as reliable, in this case at least, as the method of distillation. In the latter it is necessary to determine the *mean* boiling-point of a solution which gives off a certain amount of distillate for analysis. Moreover the pressure variations have to be regarded in a very careful way and this in actual work complicates the experiment to a considerable extent. In the method described in this paper both boiling-points are determined simultaneously under the same pressure, and the rapidity of the operation is such that a complete determination of the vapor-solution curve may be readily carried out in one day.

Of course if one wishes to work under pressures different from atmospheric, the apparatus will require modification. Here the necessity of excluding all possibility of leakage will require that the part of the inner tube which passes through the cork shall be immovable. It would then be necessary to have the tube made of two parts, the lower being capable of adjustment from without. This may possibly be effected by fitting permanently into the inner tube a piece of steel which being acted on by a magnet from without can allow of the lower portion B being raised or lowered at will. In such cases as this, it may be questionable whether this method is as rapid as the ordinary distillation method.

If the application of this method of vapor analysis were confined to two-component systems where both components are volatile, it would appear as if the field where it might be used was very limited; but such is not the case. The composition of the vapor phase in equilibrium with any solution containing two volatile and any number of non-volatile components may be readily examined by this method. Systems of this kind have of late been made a subject of study by Miller[1] who has shown by use of the Gibbs energy theory the intimate connection existing between solubility and partial vapor-pressures. When the bearing of the demonstration given by Miller — that it is always possible by a correct choice of the third (non-volatile) component to change the relative partial pressures of the two volatile components and hence render their separation by fractional distillation more easy — is fully appreciated, the work of the organic technical chemist will be performed on a far more intelligent basis. For instance, in the case of acetone and water, it is apparent from the relation deduced by Miller that the addition of sodium chlorid or any other non-volatile substance more soluble in water than in acetone will displace the curve of vapor composition more to the acetone side. So also in all cases where maxima or minima boiling-points occur, that is in all cases where complete fractional separation of the components by the usual operations is impossible, the displacement of the relation between the partial pressures of the two volatile components may probably be readily effected by the choice of a third whose solubilities in the two volatile components is widely different. In any of these cases the comparative value of the different salts in changing the partial pressures may be easily tested by the use of the apparatus described in this paper.

The relation of the curves representing vapor and solution phases under varying pressure has not, so far as the writer is aware, been made the subject of an experimental study, with the exception of one isolated case. In this case Brown[2] studied the relative composition of vapor and solution phases under the

[1] Jour. Phys. Chem. **1**, 633 (1897).
[2] Jour. Chem. Soc. **39**, 304 (1881).

pressures of 760 mm and 430 mm and came to the conclusion that the pressure term does not appear as a factor in the equilibrium. When his results are plotted in the manner used in this paper, it seems as if the relative positions of the curves were displaced in such a way that decrease of pressure caused the vapor and solution curves to approach each other; but the lack of experimental data prevents the drawing of definite conclusions on this point. The subject is of importance since it deals with the question whether the effectiveness of a fractional distillation attains its maximum under increased or under reduced pressure.

If the vapor composition be accurately determined one may readily calculate the partial pressures of the several components if the assumptions be made that Henry's law holds and that each component exists in the vapor in its normal state. From the partial pressures, especially those for dilute solutions, the molecular weight of the dissolved substance may be calculated from the van 't Hoff-Raoult formula. It is expected that the calculation of these pressures and the comparison of other relations may form the basis for a subsequent paper when measurements on the vapor-pressures of acetone-water mixtures shall have been completed.

In the present paper has been given:

1. The description and preliminary tests of an apparatus for rapid vapor analysis.

2. Its advantages and probable errors.

3. The objections which are to be raised against the employment of the Beckmann boiling-point apparatus when both components are volatile.

4. A new method of determining the purity of an organic compound by means of boiling-point comparisons.

5. Comments on the maximum effectiveness of fractional distillation.

6. The advantages and a possible error in the use of Brown's constant temperature still-head.

To Professor Bancroft at whose suggestions and under whose direction this subject has been examined, the writer expresses his thanks.

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ON MAXWELL'S THEOREM

BY PAUL SAUREL

The object of the present note is to give a demonstration of the theorem that the sum of the areas included between the actual and the theoretical isotherms is equal to zero, provided the areas above the actual isotherm are reckoned positive and those below negative. Originally, the theorem referred to the isotherms of a substance containing a single component, but it has been extended by Blümcke[1] to the isotherms of a substance containing two or more components, and a demonstration of the generalized theorem has recently been given by Duhem.

Consider a heterogeneous mass M, consisting of n components of masses $\mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_n$ and existing in the form of r homogeneous phases. If we denote the energy, entropy, volume, temperature, pressure, and masses of the components, of the i-th phase, by E_i, H_i, V_i, t_i, p_i, $\mathrm{M}_{i2}, \ldots, \mathrm{M}_{in}$ (so that M_{ij} denotes the mass of the j-th component in the i-th phase), we shall have the relation[2]

$$d\mathrm{E}_i = t_i d\mathrm{H}_i - p_i d\mathrm{V}_i + \lambda_{i1} d\mathrm{M}_{i1} + \lambda_{i2} d\mathrm{M}_{i2} + \cdots + \lambda_{in} d\mathrm{M}_{in}. \quad (1)$$

In order that the various phases should coexist it is necessary[3] that

$$\begin{aligned} t_1 &= t_2 = \cdots = t_r = t \\ p_1 &= p_2 = \cdots = p_r = p \\ \lambda_{11} &= \lambda_{21} = \cdots = \lambda_{r1} = \lambda_1 \\ \lambda_{12} &= \lambda_{22} = \cdots = \lambda_{r2} = \lambda_2 \\ &\cdots \\ \lambda_{1n} &= \lambda_{2n} = \cdots = \lambda_{rn} = \lambda_n. \end{aligned}$$

[1] Blümcke. Zeit. phys. Chem. **6**, 153 (1890).

[2] Gibbs. On the Equilibrium of Heterogeneous Substances, p. 116.

[3] Gibbs. Ibid. p. 119.

Taking the sum of the r equations of the form (1), and writing

$$\mathrm{E} = \Sigma \mathrm{E}_i, \quad \mathrm{H} = \Sigma \mathrm{H}_i, \quad \mathrm{V} = \Sigma \mathrm{V}_i,$$
$$\mathfrak{M}_1 = \Sigma \mathrm{M}_{i1} \quad \mathfrak{M}_2 = \Sigma \mathrm{M}_{i2}, \quad \ldots, \quad \mathfrak{M}_n = \Sigma \mathrm{M}_{in},$$

we shall have, for the whole mass,

$$d\,\mathrm{E} = t d\,\mathrm{H} - p d\,\mathrm{V} + \lambda_1 d\mathfrak{M}_1 + \lambda_2 d\mathfrak{M}_2 + \ldots + \lambda_n d\mathfrak{M}_n. \quad (2)$$

Moreover, as the energy is a homogeneous function of the first degree of the entropy, volume, and masses of the components, we have

$$\mathrm{E} = t\mathrm{H} - p\mathrm{V} + \lambda_1 \mathfrak{M}_1 + \lambda_2 \mathfrak{M}_2 + \ldots + \lambda_n \mathfrak{M}_n. \quad (3)$$

If we write

$$\epsilon = \frac{\mathrm{E}}{\mathrm{M}}, \quad \eta = \frac{\mathrm{H}}{\mathrm{M}}, \quad v = \frac{\mathrm{V}}{\mathrm{M}}, \quad c_1 = \frac{\mathfrak{M}_1}{\mathrm{M}}, \quad c_2 = \frac{\mathfrak{M}_2}{\mathrm{M}}, \quad \ldots, \quad c_n = \frac{\mathfrak{M}_n}{\mathrm{M}},$$

equations (2) and (3) become

$$\begin{aligned} \mathrm{M} d\epsilon + \epsilon d\mathrm{M} &= \mathrm{M}(t d\eta - p dv + \lambda_1 dc_1 + \lambda_2 dc_2 + \ldots + \lambda_n dc_n) \\ &\quad + (t\eta - pv + \lambda_1 c_1 + \lambda_2 c_2 + \ldots + \lambda_n c_n) d\mathrm{M}, \\ \epsilon &= t\eta - pv + \lambda_1 c_1 + \lambda_2 c_2 + \ldots + \lambda_n c_n, \end{aligned}$$

and consequently

$$d\epsilon = t d\eta - p dv + \lambda_1 dc_1 + \lambda_2 dc_2 + \ldots + \lambda_n dc_n. \quad (4)$$

This equation connects the changes in the average energy, entropy, volume and concentrations during any actual change in the system.

On the other hand, if we denote the energy, entropy, volume, temperature, pressure, and masses of the components, of the unit of mass of the ith phase, by ϵ_i, η_i, v_i, t_i, p_i, m_{i1}, m_{i2}, $\ldots$, m_{in}, the reasoning which served to establish equation (1) will also serve to establish the equation

$$d\epsilon_i = t_i d\eta_i - p_i dv_i + \mu_{i1} dm_{i1} + \mu_{i2} dm_{i2} + \ldots + \mu_{in} dm_{in}. \quad (5)$$

ϵ_i is thus a function of η_i, v_i, m_{i1}, m_{i2}, $\ldots$, m_{in}; and we shall assume that the functions obtained in this manner for the various phases are not distinct functions but are parts of one and the same uniform analytical function. If, then, the system undergoes a transformation by which it passes from one homogeneous

phase to a second homogeneous phase, we may calculate the change in the energy either by equation (4) or by equation (5). If, in particular, we suppose the transformation to take place at constant temperature and with constant concentrations, we shall have from equation (4),

$$\epsilon_2 - \epsilon_1 = t(\eta_2 - \eta_1) - \int_1^2 p dv,$$

and from equation (5)

$$\epsilon_2 - \epsilon_1 = t\,(\eta_2 - \eta_1) - \int_1^2 p_i dv_i.$$

A comparison of these equations yields

$$\int_1^2 p dv = \int_1^2 p_i dv_i;$$

and since p and v are the pressure and volume along the actual isotherm, and p_i and v_i are the pressure and volume along the theoretical isotherm, the theorem is demonstrated.

Bordeaux, January 23, 1899

TERNARY MIXTURES, IV

BY WILDER D. BANCROFT

Practically the only extended study of conjugate solutions is that made by Wright, alone and in collaboration with others.[1] This work consisted in a determination of isotherms for systems composed of two partially miscible metals and a third metal consolute with each of the others. It is easy to pick flaws in the experimental work. Wright, himself, has pointed out its shortcomings with great clearness and his statement is recapitulated here solely to show that the conclusions to be deduced in this paper from that work cannot be accepted as final until the measurements have been repeated under more favorable circumstances. The metals used were not always pure, the aluminum containing over four percent of iron and silicon.[2] These impurities were allowed for in the analyses so that the tabulated data give the gram percentages of each of the three metals forming the ternary mixture ; but we are not able in any way to foretell the effect of the impurities upon the distribution ratios. The temperatures were not constant during the experiments, fluctuations of one hundred degrees not being excluded. From some experiments that were made it appears that the error due to the actual temperature difference between two measurements was probably not so serious as those due to changes of temperature in a single experiment, the convection currents thus generated preventing the reaching of equilibrium. The most serious source of error, however, occurred in the method adopted for separating the two phases. The two liquid layers were not drawn off at the temperature of the experiment and then analyzed. Instead of this,

[1] Wright and Thompson. Proc. Roy. Soc. **45**, 461 (1889) ; **48**, 25 (1890); **49**, 156 (1891) ; Wright, Thompson and Leon. Ibid. **49**, 174 (1891) ; Wright. Ibid. **50**, 372 (1891) ; **52**, 11 (1892) ; **52**, 530 (1893) ; **55**, 130 (1894).

[2] Wright. Ibid. **52**, 12 (1892).

the whole mass was cooled as rapidly as possible, the upper and lower portions of the ingot being then analyzed. When one recalls the difficulties to be overcome in making a homogeneous casting with only two metals, one can easily see that this method of analysis can be justified only on the ground taken by Wright—that he could find no better method. As a matter of fact, attempts to draw off the molten solutions proved unsatisfactory.[1] That the method of rapid cooling cannot give accurate results is shown by two facts. We know from the phase rule that all mixtures corresponding to points on a given tie-line must separate into the same two liquid phases provided the system is allowed to reach equilibrium. This was apparently not the case in the experiments of Wright and Thompson.[2] The second point is that with mixtures that did not separate into two liquid phases and which should therefore have been homogeneous, differences in composition between the upper and the lower portions of the ingot were found, amounting in one case to over two percent.[3]

In view of the numerous sources of error it is not surprising to find that increasing the amount of the consolute metal does not always produce an increase in the solubility of the partially miscible metals. Instead of this there are annoying fluctuations which, though evidently due to experimental error, are still sufficient to make the application of the mass law formulas to the isotherm an extremely unsatisfactory proceeding. On the other hand these variations produce relatively less effect on the distribution ratio. For this reason I shall limit myself, in this paper, to a discussion of the equilibrium between the solution phases. It has been shown[4] that, for two non-miscible liquids, A and B, and a third, C, consolute with the other two, the distribution of the third liquid between the other two can normally be represented by the formula

$$\left(\frac{C_1}{A_1}\right)^n \div \frac{C_2}{B_2} = \textit{constant}.$$

[1] Wright and Thompson. Proc. Roy. Soc. **45**, 470 (1889).
[2] Ibid. **49**, 192 (1891).
[3] Wright and Thompson. Ibid. **45**, 463 (1889).
[4] S. F. Taylor. Jour. Phys. Chem. **1**, 471 (1897).

In this equation C_1 and C_2 refer to the amounts of the consolute liquid in the two phases while A_1 is the amount of the component A in the phase in which it is the solvent and B_2 is the amount of the component B in the phase in which it is solvent, these amounts being expressed in any units whatsoever. The exponential factor n is not necessarily an integer. So far, no hypothesis has yet been advanced enabling us to predict the value of this exponential factor in any one case. If the logarithm of C_1/A_1 be measured along one axis and the logarithm of C_2/B_2 along the other, the resulting curve is a straight line provided the above equation describes the facts. This graphical method is the easiest and quickest method of determining whether or not a given set of data conforms to the mass law, and the direct measurement of the pitch of the curve is by far the simplest method of getting at the value of the exponential factor.

The data of Wright and Thompson are reproduced graphically in Fig. 1. The coordinates are the logarithms of the concentrations, these latter being expressed in grams of the consolute metal per gram of the solvent metal. In order to prevent overlapping, the origin is in a different place for each curve; but the scale is the same for all, each division being equal to 0.2. The curves are so labelled that the middle metal is the consolute one. The concentrations of the consolute metal in the first metal are measured along the ordinates and the concentrations in the last metal of the three along the abscissas. Curves are given for lead, silver and zinc[1]; bismuth, tin and zinc[2]; zinc, cadmium and bismuth[3]; cadmium, tin and aluminum[4]; aluminum, tin and bismuth[5]; aluminum, silver and lead[6]; aluminum, silver and bismuth[7]; aluminum, tin and lead[8]; zinc, silver and

[1] Proc. Roy Soc. **50**, 391 (1891).
[2] Ibid. **50**, 388 (1891).
[3] Ibid. **52**, 536 (1892).
[4] Ibid. **55**, 132 (1894).
[5] Ibid. **52**, 19 (1892).
[6] Ibid. **52**, 22 (1892).
[7] Ibid. **52**, 24 (1892).
[8] Ibid. **52**, 16 (1892).

bismuth.[1] It must be remembered in considering this diagram

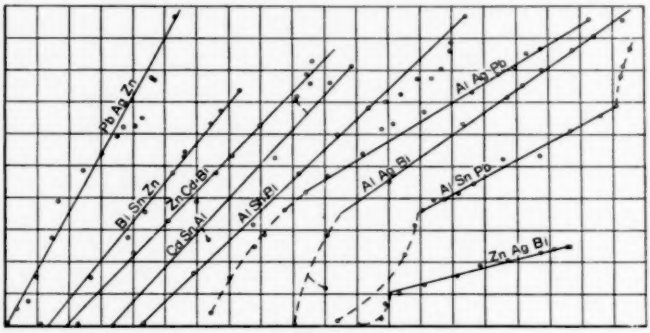

Fig. 1

that a very slight error causes a large displacement at the lower ends of the curves. For instance an error of less than one-half of one percent would make the aluminum, silver and lead curve a straight line. It is evident at once that all these systems are normal though there are some curious variations to which attention must be called. With lead, silver and tin and with aluminum, tin and bismuth, the curves sweep out and back just before the crest-point[2] is reached. It is probable that from such disturbances conclusions might be drawn as to the relative positions of the boundary curves; but I have not yet succeeded in getting any satisfactory results in this way. The sudden apparent change of direction at the upper end of the aluminum, tin and lead curve is quite unintelligible.

The same data are tabulated in Tables I–XII. The figures are given for only two of the metals in each phase, for the solvent metal and the consolute metal. Since the values given are grams per hundred grams of the alloy the amounts of the third metal can readily be determined by subtraction. The subscripts one and two refer to the denser and the less dense phase respectively. In the sixth column are the values of the constant as calculated from the formula at the head of each table. No cor-

[1] Proc. Roy. Soc. **50**, 393 (1891).

[2] Snell. Jour. Phys. Chem. **2**, 470 (1898).

rections have been made for the partial miscibility of the two hypothetically non-miscible metals even though bismuth is soluble up to fifteen percent or thereabouts in zinc. No formulas are given in the last three tables because it was evident that the data were so abnormal that it was useless to try to apply the theory. The bracketed figures are the data for the crest-points. They were not observed directly; but were obtained by extrapolation.

TABLE I

$$\left(\frac{Sn_1}{Bi_1}\right) \div \left(\frac{Sn_2}{Zn_2}\right)^{1.25} = K$$

Temperature about 650°

Sn_1	Bi_1	Sn_2	Zn_2	Sn_1/Sn_2	K
0.00	85.72	0.00	97.68		
3.23	80.27	1.98	94.57	1.63	5.05
6.35	75.82	3.97	91.82	1.60	4.25
10.38	70.52	6.35	88.12	1.63	3.94
13.53	66.33	7.95	85.54	1.70	3.97
19.09	51.35	11.19	80.13	1.71	4.33
20.80	46.01	12.72	77.56	1.64	4.33
20.44	42.43	12.98	77.32	1.57	4.48
21.89	30.33	17.25	70.83	1.27	4.21
22.37	25.94	19.16	67.80	1.17	4.19
[21.5	18.5	21.5	60.0]	1.00	4.20

TABLE II

$$\left(\frac{Ag_2}{Zn_2}\right)^{1.8} \div \left(\frac{Ag_1}{Pb_1}\right) = K$$

Temperature 750°–850°

Ag_1	Pb_1	Ag_2	Zn_2	Ag_2/Ag_1	K
1.25	96.69	38.91	57.97	31.1	34.8
1.54	96.28	40.89	55.73	26.6	36.0
1.71	96.43	45.01	51.62	26.3	44.0
2.39	95.78	47.68	48.58	20.0	38.8
4.18	94.43	52.80	43.11	12.7	28.1
5.55	93.16	54.93	40.86	9.9	28.8
10.22	88.02	60.14	30.86	5.9	28.6
12.62	85.38	63.70	25.00	5.1	36.2
15.69	81.88	65.34	20.79	4.2	40.9
17.43	80.15	65.94	19.27	3.8	42.1
17.65	79.78	67.03	16.49	3.8	44.8
19.51	78.54	63.79	13.92	3.3	61.2
29.53	68.03	60.35	11.23	2.1	47.8
29.90	67.21	59.32	11.53	2.0	38.1
[45.5	48.2	45.5	6.3]	1.0	32.6

TABLE III

$$\left(\frac{Cd_1}{Bi_1}\right) \div \left(\frac{Cd_2}{Zn_2}\right)^{0.96} = K$$

Temperature about 600°

Cd_1	Bi_1	Cd_2	Zn_2	Cd_1/Cd_2	K
0.00	85.72	0.00	97.68		
6.98	78.84	3.77	92.91	1.85	1.92
14.27	71.34	9.80	85.74	1.46	1.64
21.19	64.38	14.37	80.09	1.48	1.71
28.24	56.75	18.04	75.94	1.57	1.98
33.67	50.34	24.48	69.18	1.37	1.81
38.06	46.02	29.32	63.78	1.30	1.74
46.20	37.08	37.42	55.57	1.24	1.82
53.88	24.93	46.73	44.20	1.15	1.62
54.48	21.21	49.73	37.97	1.09	1.96
53.08	21.55	50.93	33.82	1.04	1.66
[52.0	19.5	52.0	28.5]	1.00	1.50

TABLE IV

$$\left(\frac{Sn_1}{Cd_1}\right)^{0.92} \div \left(\frac{Sn_2}{Al_2}\right) = K$$

Temperature 700°–750°

Sn_1	Cd_1	Sn_2	Al_2	Sn_2/Sn_1	K
0.00	99.78	0.00	96.61		
4.75	94.84	2.75	92.80	1.73	2.15
14.78	84.70	9.98	85.09	1.48	1.71
35.98	61.49	22.28	71.94	1.61	1.97
53.15	40.79	27.88	66.04	1.91	3.02
57.28	34 26	37.07	54.75	1.55	2.37
59.18	27.77	43.17	46.18	1.37	2.14

TABLE V

$$\left(\frac{Sn_1}{Bi_1}\right) \div \left(\frac{Sn_2}{Al_2}\right)^{1.05} = K$$

Temperature 750°–850°

Sn_1	Bi_1	Sn_2	Al_2	Sn_1/Sn_2	K
0.00	99.72	0.00	97.98		
2.79	96.64	2.45	95.15	1.14	1.35
5 57	93.58	4.90	92.35	1.14	1.30
12.26	86.03	9.43	87.51	1.30	1.47
21.02	76.90	17.56	78.94	1.20	1.33
31.37	65.19	26.40	68.33	1.19	1.31
40.76	54.37	34.18	58.83	1.19	1.33
46.13	47.60	35.63	56.28	1.29	1.56
50.09	41.64	38.12	53.51	1.32	1.72
54.22	35.82	42.80	48.11	1.27	1.71
56.91	30.73	42.97	47.54	1.32	2.06
57.61	27.10	45.76	44.71	1.26	2.08
58.17	24.01	49.48	37.44	1.18	1.84
57.23	23.20	51.32	34.31	1.12	1.61
[55.75	18.60	55.75	25.65]	1.00	1.32

TABLE VI

$$\left(\frac{Ag_2}{Al_2}\right)^{1.65} \div \left(\frac{Ag_1}{Pb_1}\right) = K$$

Temperature 830°–900°

Ag_1	Pb_1	Ag_2	Al_2	Al_2/Al_1	K
0.00	99.93	0.00	98.09		
0.30	99.61	15.05	83.35	50.2	20
0.61	99.24	31.98	66.05	51.3	49
0.80	99.01	43.15	54.58	54.0	84
1.13	98.59	53.85	44.03	47.8	122
1.31	98.40	58.43	39.69	44.7	142
1.74	98.10	66.40	31.50	38.1	193
2.32	97.47	71.07	26.10	29.3	220
3.16	96.53	75.33	22.04	23.8	232
5.19	94.61	80.37	16.78	15.1	242
6.69	93.18	84.34	12.38	12.6	330
7.87	91.99	84.63	11.54	10.8	313
11.75	88.14	84.91	9.69	7.2	270
20.99	78.87	83.10	7.17	4.0	215
28.15	71.55	81.17	5.36	2.9	225
32.82	66.77	77.64	4.61	2.4	215
36.40	62.85	74.65	3.70	2.3	246
40.73	58.31	72.88	3.36	1.8	232
[58.25	40.00	58.25	1.75]	1.0	223

TABLE VII

$$\left(\frac{Ag_2}{Zn_2}\right)^{3.8} \div \left(\frac{Ag_1}{Bi_1}\right) = K$$

Temperature 700°–800°

Ag_1	Bi_1	Ag_2	Zn_2	Ag_2/Ag_1	K
5.08	79.28	37.06	57.60	7.3	3.7
6.84	77.24	38.80	55.27	5.8	3.0
7.58	78.58	43.16	48.85	5.7	6 5
8.98	77.99	46.31	45.02	5.1	9.7
12.71	76.19	47.94	42.01	3.8	10.0
18.68	68.97	49.92	37.66	2.7	10 8
22.96	62.72	51.34	34.32	2.2	12.4
29 26	53.10	51.16	31.63	1.8	11.3
37.33	43.27	49.73	27.49	1.3	11.1
41.22	38.52	47.15	24.09	1.14	11.9
43.74	33.82	45.25	22.64	1.04	10.7
[44.63	33.12	44.63	22.25]	1.00	10.5

Table VIII

$$\left(\frac{Ag_2}{Al_2}\right)^{1.43} \div \left(\frac{Ag_1}{Bi_1}\right) = K$$

Temperature 830°–900°

Ag_1	Bi_1	Ag_2	Al_2	Ag_2/Ag_1	K
0.00	99.72	0.00	97.98		
0.74	98.39	12.30	85.04	16.6	8.4
1.59	97.43	24.20	72.31	15.2	8.1
1.95	97.31	33.95	62.55	17.4	20.8
2.01	97.49	51.80	44.81	25.8	61.1
4.81	94.72	68.63	27.43	14.3	75.0
11.51	88.09	81.29	14.00	7.2	75.3
21.56	77.72	83.75	9.80	3.8	77.6
25.41	74.07	83.88	8.14	3.3	81.8
31.05	68.28	82.60	7.44	3.0	83.6
40.92	57.97	75.64	5.66	1.8	57.7
48.53	49.62	68.16	3.34	1.4	76.4
[58.25	39.50	58.25	2.25]	1.0	71.8

TABLE IX

$$\left(\frac{Sn_1}{Pb_1}\right) \div \left(\frac{Sn_2}{Al_2}\right)^{1.85} = K$$

Temperature 750°–850°

Sn_1	Pb_1	Sn_2	Al_2	Sn_2/Sn_1	K
0.00	99.93	0.00	98.09		
4.60	95.33	6.25	91.89	1.36	6.97
11.17	88.77	14.50	83.17	1.30	3.19
12.51	87.43	20.26	77.52	1.62	1.71
14.01	85.75	24.50	72.95	1.75	1.23
15.97	83.61	27.00	70.01	1.69	1.11
18.25	81.42	27.47	69.64	1.51	1.25
21.13	78.40	28.98	67.63	1.37	1.32
25.10	74.17	31.83	64.79	1.27	1.25
33.64	65.35	39.37	55.61	1.17	0.98
45.41	51.89	45.34	49.08	1.00	1.02
55.16	39.73	48.11	46.11	0.87	1.29
61.52	29.14	52.27	40.57	0.85	1.32
64.21	24.52	54.62	36.00	0.83	1.21
65.07	23.06	59.14	25.86	0.91	0.60
63.92	21.78	60.27	22.69	0.94	0.48
[62.6	19.4	62.6	18.0]	1.00	0.32

TABLE X

Temperature about 650°

Sn_1	Pb_1	Sn_2	Zn_2	Sn_2/Sn_1
0.00	98.76	0.00	98.86	
4.45	93.79	6.64	90.75	1.49
6.94	91.01	9.91	86.71	1.43
9.60	87.91	13.47	82.18	1.40
12.60	83.74	16.68	78.48	1.32
14.76	81.02	19.27	75.36	1.31
16.11	79.16	20.35	73.51	1.27
18.71	75.67	22.51	70.04	1.20
21.95	70.48	25.07	66.72	1.14
26.28	60.48	27.49	62.33	1.04
29.43	53.81	28.64	59.94	0.97
31.63	48.64	29.58	57.87	0.94
33.88	43.76	30.33	56.25	0.90
35.03	39.59	30.24	55.33	0.87
35.65	29.10	32.85	48.51	0.92
[35.0	22.5	35.0	42.5]	1.00

TABLE XI

Temperature 550°–650°

Cd_1	Pb_1	Cd_2	Zn_2	Cd_2/Cd_1
0.00	98.76	0.00	98.86	
5.17	92.85	10.12	88.34	1.91
13.45	83.89	24.91	72.65	1.85
17.57	80.18	31.48	65.67	1.79
19.14	78.73	36.50	60.01	1.91
21.44	76.34	46.42	47.62	2.17
22.68	75.13	55.72	34.12	2.46
22.23	76.32	59.20	27.36	2.66
22.37	76.31	70.78	11.05	3.17
23.70	74.85	72.76	8.44	3.07
33.80	64.35	72.06	6.72	2.13
46.93	50.82	69.50	4.64	1.48
50.30	47.45	67.67	4.04	1.34
[60.6	36.5	60.6	2.9]	1.00

TABLE XII

Temperature 600°–700°

Sb_1	Pb_1	Sb_2	Zn_2	Sb_2/Sb_1
0.00	98.79	0.00	98.86	
2.69	93.87	4.60	93.13	1.71
7.11	87.02	11.41	81.06	1.60
8.37	85.22	16.75	69.73	2.00
9.77	80.81	22.33	60.21	2.29
15.45	67.17	26.68	48.98	1.73
21.00	53.65	27.11	43.34	1.29
[26.5	38.1	26.5	35.4]	1.00

Nernst's distribution law was deduced under the explicit proviso that there is no passage of either non-miscible liquid into the other phase on addition of the third component. This condition is not satisfied in any of these systems. Since the distribution ratio at the crest-point must be unity, it is obvious that the ratio can remain constant only in case the ratio at infinite dilution is also unity—a condition which is rarely fulfilled. From this it follows that when the third substance is a liquid no really accurate conclusion as to its reacting weight can be drawn from a study of the distribution ratio—in the pres-

ent state of our knowledge. In spite of these facts, the distribution ratio does remain remarkably constant in a number of cases over a surprising range of concentrations. For this and other reasons I have calculated the distribution ratio for the twelve systems considered and have given the results in the fifth column of the tables. It seemed best to take the concentrations expressed in grams per hundred grams of the phase because this was as near to volume concentrations as one could get and also because this gave better results than any other method available. To have expressed the concentrations in grams per hundred grams of the solvent metal would merely have made the results in the fifth column a bad imitation of those in the sixth, which certainly would not have helped the cause of science.

Surprisingly good constants are obtained with tin in bismuth and zinc; with cadmium in zinc and bismuth (Table III); with cadmium in tin and aluminum; with tin in aluminum and bismuth. With bismuth, tin and zinc (Table I), the rate remains practically constant until there is over twenty percent of tin in the bismuth phase and thirteen percent in the zinc phase, the mean value being 1.63. With cadmium, tin and aluminum (Table IV), the ratio varies irregularly until there is fifty-seven percent of tin in the cadmium phase and thirty-seven percent in the aluminum phase. In this particular system the solvent action of the tin is very slight, there being less than nine percent of cadmium in the aluminum phase and an equally small quantity of aluminum in the cadmium phase in the conjugate solutions just cited. This, however, seems not to be an essential feature because the distribution ratio of tin in bismuth and aluminum (Table V) remains practically constant until there is fifty-seven percent of tin in the bismuth phase and fifty-one percent in the aluminum phase while, at the same point, there is nearly twenty percent of aluminum in the bismuth phase and about fourteen percent of bismuth in the aluminum phase.

Very bad distribution ratios are obtained for silver in lead and zinc, in lead and aluminum, in bismuth and aluminum, and in bismuth and zinc (Table VII) if we consider any great range of

concentrations. For silver in lead and aluminum (Table VI) or bismuth and aluminum (Table VIII) the distribution ratio remains about constant for the first three concentrations and that is all. To bring silver in zinc and lead (Table II) even approximately into line would require the assumption of Ag_6 in zinc.

With tin in lead and aluminum (Table IX) and in lead and zinc (Table X), the distribution ratio changes its sign with increasing concentration, being first greater than unity, then less than unity, becoming unity again at the crest-point. It seems very probable that this is due to experimental error; but one cannot be certain of this until the experiments have been repeated by someone, especially since the variation appears to lie completely outside any experimental error. For the present, therefore, it is a case of possibly inexact theory against possibly inaccurate measurements.[1] With cadmium (Table XI) or antimony (Table XII) in zinc and lead we have the reverse phenomenon of a sharp increase in the value of the distribution ratio, the value of course falling to unity at the crest-point.

When the value of the distribution ratio remains constant, it is equal to the ratio of the solubilities provided the third substance is a solid. When the third component is a liquid we have no way even of guessing at the value of the distribution ratio at infinite dilution unless we make use of the van't Hoff-Raoult formula $n/N = \log p/p_1$. No one would claim that this formula would hold accurately for extreme concentrations since it is limited explicitly to cases in which the component whose vapor-pressure does not enter into the formula may be treated as an ideal gas. On the other hand it was conceivable that the variations might be approximately the same for two different metals so that the ratios of the concentrations might remain constant. If this were the case the distribution ratio at infinite dilution would be equal to the inverse ratio of the reacting weights of the two non-miscible liquids. To see how far this might hold I have calculated these values and compared them

[1] Such a variation does take place in certain systems where polymerization and dissociation are possible. Cf. Jakowkin. Zeit. phys. Chem. **18**, 589 (1895).

with the distribution ratios as obtained from the most dilute solutions given in Tables I–XII. The results are tabulated in Table XIII, the values in parentheses being taken from data by Wright for systems in which the isotherm was obviously distorted by the separation of a compound on cooling. The ratios are given to the nearest tenth.

TABLE XIII

	Pb/Zn	Bi/Zn	Pb/Al	Bi/Al	Cd/Al
Calculated	3.2	3.2	7.6	7.7	4.1
Sn found	1.5	0.6	1.4	0.9	1.7
Ag found	31.1	7.3	50.2	16.6	
Cd found	1.9	0.5			
Sb found	1.7	(0.3)	(3.3)	(2.6)	

Although the 'found' values are not those at infinite dilution, I have convinced myself that extrapolation would not help matters any. On the other hand, experimental error may play a relatively large part since a small percentage error in the composition of the phases would have a very large effect on the composition of the phases. For this reason as well as for others already mentioned, it is very much to be desired that these systems should be studied again under the most favorable instead of under the least favorable circumstances. Taking the data as they stand, it is obvious that in no case do the 'calculated' values agree with those found by direct experiment. For the present, therefore, we have no method even of approximating the initial value of the distribution ratio when the third component is a liquid. I have laid what may seem to be undue stress on this point because it has been ignored with surprising consistency in the past.[1]

Ostwald's position in regard to the matter is distinctly unsatisfactory.[2] He first takes up the case where the third substance is a solid and answers Berthelot's claim that the distribution coefficient for a saturated solution is not the same as the ratio of the solubilities in the following manner: "It is easy to

[1] See, however, Tammann. Zeit. phys. Chem. **22**, 481 (1897).

[2] Lehrbuch, I, 811.

see, however, that as a matter of fact, the ratio of the solubilities and the distribution ratio must be identical. For let us imagine as much succinic acid added to a mixture of ether and water as this will dissolve, each of the two solutions will, after separation, be saturated with respect to succinic acid, and will at the same time be in equilibrium, since neither can take succinic acid from the other; the ratio of the two concentrations is therefore simultaneously that of solubility and of distribution." This is open to criticism. It is a fair answer to Berthelot; but is not quite a fair statement of the case because it ignores the fact that if two non-miscible liquids are saturated separately with a solid the solutions will not be in equilibrium (theoretically at any rate) if mixed. In the instance cited by Ostwald of ether, water and succinic acid, no reference is made to the fact that the ratio of ether to water in each of the phases cannot be the same after saturation with succinic acid as when no succinic acid is present. The difference may be very slight owing to the slight solvent action of succinic acid and its low solubility in water; but the fact that there is a change should not be ignored by anyone interested in exact theory. Ostwald then goes on: "Berthelot makes a further argument intended to prove *a priori* the impossibility of such an identity. With bromin in water and carbon bisulfid the distribution coefficient has at each moment a finite value, while the solubility of bromin in carbon bisulfid and therefore the ratio of its solubility to the solubility in water is unlimited. This difficulty disappears if we give up the definition of the distribution ratio, selected for convenience only, which refers this value to equal volumes of the solutions and substitute for it the more rational reference to equal quantities of the solvent. If one takes the distribution coefficient as the ratio of the amounts of the solute in equal quantities of the two solvents, then in the case that the dissolved substance is infinitely miscible with one of the solvents the distribution coefficient will also be infinite for a saturated solution, that is one containing an infinite amount of the dissolved substance." This leaves the really important point untouched and is not strictly accurate in

the part that is taken up. If an infinite amount of bromin be added there will be only one solution and not two, because the solubility of water in bromin, though slight, is not zero. The important point, however, is the question why the distribution ratio of bromin in carbon bisulfid and water should have such a relatively low value for dilute solutions of bromin. In regard to this we have, as yet, no theory whatsoever, chiefly because no one has studied the application of Henry's law to mixtures of liquids, nor the way in which the system passes from concentrations for which Henry's law holds more or less accurately to concentrations for which the van't Hoff-Raoult formula holds more or less accurately.

The general results of this paper are:

1. Within the limits of experimental error the formula $\left(\frac{C_1}{A_1}\right)^n \div \left(\frac{C_2}{B_2}\right) = constant$ describes the equilibrium between conjugate solutions for a number of systems consisting of three metals.

2. With the exception of cadmium or antimony in zinc and lead the distribution ratio does not exceed two for any system not containing silver when the concentrations are expressed in grams per hundred grams of the two phases.

3. The distribution ratio for dilute solutions stands in no obvious relation to the reacting weights of the partially miscible metals.

Cornell University

A DEMONSTRATION OF TWO THEOREMS OF ELECTROSTATICS

BY PAUL SAUREL

Denoting the electrical energy of a system of electrified points by W, we have

$$W = \sum \frac{q_m q_n}{r_{mn}}$$

$$= \tfrac{1}{2} \Sigma V_m q_m,$$

q_m, q_n being the charges at the points m, n; r_{mn} the distance between these points; and V_m the potential at the point m. From this,

$$dW = \tfrac{1}{2} \Sigma V_m dq_m + \tfrac{1}{2} \Sigma q_m dV_m. \qquad (1)$$

Consider the work $d\mathcal{T}$ done by the electrical forces during a small displacement. We shall have

$$d\mathcal{T} = \sum \frac{q_m q_n}{r^2_{mn}} dr_{mn}$$

$$= -\sum q_m q_n d\frac{1}{r_{mn}}$$

$$= -d \sum \frac{q_m q_n}{r_{mn}} + \sum \frac{q_m dq_n + q_n dq_m}{r_{mn}}$$

$$= -dW + \Sigma V_m dq_m. \qquad (2)$$

By the aid of (1), this becomes

$$d\mathcal{T} = dW - \Sigma q_m dV_m; \qquad (3)$$

and by adding (2) and (3) we get

$$d\mathcal{T} = \tfrac{1}{2} \Sigma V_m dq_m - \tfrac{1}{2} \Sigma q_m dV_m. \qquad (4)$$

There are three cases of interest:

(1) $d\,V_m = 0$;
$d\,\mathcal{T} = d\,W$. (Maxwell's Theorem)

(2) $dq_m = 0$;
$d\,\mathcal{T} = -d\,W$.

(3) $d\,\mathcal{T} = 0$;
$d\,W = \Sigma V_m dq_m = \Sigma q_m d\,V_m$.

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NEW BOOKS

The Elements of Physical Chemistry. *By J. L. R. Morgan. First edition. 13 × 19 cm; pp. viii and 299. New York: John Wiley and Sons, 1899. Price: cloth $2.00.* — In the preface the author says: "The object of this book is to present the elements of the entire subject of Physical Chemistry in one volume, together with the important and but little known applications of it to the other branches of chemistry. Many persons have found it difficult to obtain a comprehensive outline of the subject, owing to the length of time which it has been necessary to spend upon the separate volumes devoted to special portions of it. To all such this volume may be of value. ... The arrangement as well as the scope of the volume is new, which I think makes the subject more logical and clear."

The successive chapters are entitled: introductory remarks; the gaseous state; the liquid state; the solid state; solution; the rôle of the ions in analytical chemistry; thermochemistry; chemical change (equilibrium, then reaction velocity); phases; electrochemistry (migration of the ions, conductivity of electrolytes, electromotive force, electrolysis and polarization). This classification does not differ materially from that adopted by Nernst. Thermochemistry is placed before the mass law (which however is referred to in the second chapter) and the section in Nernst's book entitled "atom and molecule" has been absorbed; but otherwise there is not much change. The classification cannot be called a good one. Dissociating gases are a case of chemical equilibrium but they are discussed early in the book, long before the mass law has been taken up. The boiling-point and freezing-point methods involve thermochemical data and these latter are discussed two chapters later. The phase rule comes just before electrochemistry as in the first edition of Nernst's *Theoretische Chemie*. The influence of Nernst rather than of Ostwald is to be detected in the unfortunate prominence of kinetic theory throughout the volume.

This classification is no worse than those in other text-books and has much the same faults. There is a curious disinclination on the part of physical chemists to recognize the fact that their science has grown. No one nowadays would jumble together qualitative and quantitative analysis, taking up the quantitative determinations of one group before the qualitative tests for the second, yet we pride ourselves on doing just that thing in physical chemistry. We are bound to come sooner or later to a division of the subject into qualitative and quantitative physical chemistry. The qualitative phenomena will then be classed where they belong under the phase rule and the theorem of Le Chatelier. The quantitative phenomena will be classed where they belong under the mass law and the theorem of van 't Hoff. The reviewer has a classification for quantitative physical chemistry which he has been testing for several years and which

he believes to have merits. The general arrangement is as follows. Non-electrolytes: mass law at constant temperature, thermochemistry, change of equilibrium with the temperature. Electrolytes: mass law at constant temperature, thermochemistry, change of equilibrium with the temperature. Reaction velocity at constant temperature and then with changing temperature in homogeneous and inhomogeneous systems including diffusion, vaporization and crystallization. Miscellaneous, including surface tension, etc. Electrochemistry. This classification is open to the criticism that it separates things that might well come together; but it has the advantages that each step follows naturally and logically from the preceding ones and that at no point is it necessary to presuppose what comes later. For these reasons the reviewer believes this classification, though by no means perfect, to be better than those of Ostwald, Nernst, van 't Hoff, Speyers, and Morgan.

While the author is perfectly right in stating that there is a need for a work giving the general principles of physical chemistry in one volume, it seems as though he had gone to the other extreme and attempted too great condensation. It is very difficult to compress the whole subject into less than three hundred small pages without making the treatment superficial. That one is prepared for; but, in this particular volume, the errors of commission and of omission occur on almost every page. On p. 2 we read: "Energy is the power of doing work which a body possesses by reason of its state." On p. 6 we learn how to determine the atomic weight of lead when the atomic weight of oxygen is known; but why this latter should be 16 is not discussed. When we get to p. 15 we are told that "the atomic weight of hydrogen is assumed to be 1," while on p. 16 we read: "In order to preserve the relation between the molecular weight and the density, it is customary to calculate the latter as based upon an ideal gas, the weight of which is 1/32 that of O. In this way we avoid actually using hydrogen as a standard in the experiment." The development of the gas law on p. 12 is not clear. On p. 17 the correction for the barometer refers to readings in millimeters and not in centimeters as the text implies. It is not correct to state, p. 25, that Avogadro's law holds in all cases where there is no dissociation. The author contradicts this himself ten pages later. On p. 27 the reader would get the impression that changing from pressures to concentrations did not change the numerical value of the dissociation constant.

On p. 55 is the sentence: "Should this kinetic energy of the molecules be increased by heat, then the attraction will be overcome and the liquid goes into the gaseous state, i. e. it boils." Under surface tension, p. 65, there is no reference to the question of a contact angle.

Discussing Henry's law, p. 76, the author says: "The gas absorbed in this way is not to be considered as liquefied; its molecules simply become constituents of the liquid, just as those of the latter are constituents". The calculation of the molecular weights of non-miscible liquids from the vapor-pressures of the pure components cannot be applied, p. 79, to "all mixtures that form two layers" nor is it true that "the vapor-pressure is still equal to the sum of those of the two layers." It is not true that "equal amounts of each layer must distil over at any one temperature." Pfeffer, p. 82, was not the first man to notice that a colored solution diffuses into water until the mass is homogeneous

nor was he the first to discover osmotic pressure. He was the first man to make quantitative measurements of osmotic pressure — a very different thing. On p. 94 it is unfortunate to select sodium chlorid as an instance of Ostwald's dilution law. In discussing the relation between concentration and vapor-pressure it is nowhere brought out that n is expressed in terms of the molecular weight of the solute in the solution and N in terms of the molecular weight of the solvent in the vapor. The reviewer would suggest a reference at this point to the case of acetic acid. On p. 113 the sentence "Since the ice which separates is always pure solvent" should read "When the ice which separates is pure solvent." There is no reference at all to a rise of freezing-point due to solid solutions. On p. 129 there is the incorrect definition: "A saturated solution is one which contains the maximum amount of substance."

When discussing the dissociation of hydriodic acid, p. 163, the experiments of Lemoine are cited instead of those of Bodenstein. Commenting on the fact that the catalytic action of hydrogen is not strictly proportional to the concentration, the author says, p. 199: "There must be, then, another factor to be considered, and this Arrhenius found to be the presence of other ions which increase the catalytic action of those of H. This theory explains very simply the anomalous behavior already mentioned". Contrast this with the paragraph on the change of reaction velocity, with the temperature, p. 208, where no reference is made to the van 't Hoff formula. The deduction of the phase rule on p. 210 is inaccurate.

In the chapter on electrochemistry the volt is defined, p. 215, as 10/11 of the electromotive force of the Daniell cell. On p. 216 Faraday's law is expressed as follows: "All movement of electricity in electrolytes takes place only by the concurrent movement of the ions in such a way that equal amounts of electricity cause chemically equivalent amounts of the different ions to move". A good deal of pains has evidently been spent on this definition and yet it leads to the conclusion that the migration velocities are equal in mixed solutions. The unit of conductivity is defined on p. 224 in reciprocal ohms; but the migration velocities on p. 232 are referred to the conductivity of mercury as unity. On p. 254 the author ignores Helmholtz's work on concentration cells. When discussing the theory of the accumulator, p. 283, no reference is made to Liebenow's plumbic acid theory and in the pages on polarization no reference is made to any work subsequent to that of Le Blanc so that the true significance of the decomposition point (p. 289) at 1.70 volts (1.67) is missed completely.

These defects have been pointed out at some length because these are errors that are in no way a necessary consequence of the plan of the book. It is not until these — and many others — are corrected that the usefulness of a book constructed on these lines can be discussed. *Wilder D. Bancroft*

Lectures on Theoretical and Physical Chemistry. *By J. H. van't Hoff. Translated by R. A. Lehfeldt. Part I, Chemical Dynamics. 15 × 22 cm; 254 pp. London: Edward Arnold, 1898. Price: cloth 12 shillings.* — There has already been a notice of the German original (**2**, 256) and of a French translation of this work (**2**, 565). It is with pleasure that I call attention to the English translation. The general appearance of the work is good and the

translation has been well done. One would have been even more grateful if the translator had followed the example of some other translators and had added an index. *Wilder D. Bancroft*

A Textbook of Inorganic Chemistry. *By G. S. Newth. Fifth Edition; 13 × 19 cm; pp. xv and 669. New York: Longmans, Green and Co., 1897. Price: $1.75.* — There is, apparently, an extensive demand for Mr. Newth's textbook of general chemistry; for a fifth edition is now out. The book is a big one, and presents a lot of detail. Opinions may well differ on how much matter should be provided for the study of a beginner; but it does seem to the reviewer that 650 pages are too much. The first thing to be attained should be some sort of general view of the subject, not acquaintance with a mass of detailed information. In the many details, the general view is easily lost.

The author has arranged his material in three Parts. The first of these presents general considerations; the second a study of hydrogen, oxygen, nitrogen, and carbon; and the third a systematic treatment of the elements, according to the periodic classification. It results from this that we have a disquisition upon molecules, atoms, elements and compounds, chemical affinity, valence, gas theory, dissociation, electrolysis, the periodic system, evaporation and fusion, solutions, thermochemistry, etc., for a hundred and fifty pages, before we begin to find a serious statement of elementary facts about the air, combustion, water, and the like. Now this is too bad. And it may well be questioned whether it is wise to set out, in a treatise on a science of facts, with the dogmatic statement that 'matter' is to be regarded as aggregations of molecules. Chemical facts, and the actual content of the molecular theory (which has, really, nothing to do with discrete 'molecules'), and the meaning of the combining weights of elements, can all be clearly and simply put without entangling them in a network of hypotheses that are independent of them.

And a better arrangement of the material, the reviewer thinks, could be attained by presenting the significant experimental and theoretical — not hypothetical — facts of the science in the natural order in which these elements of the matter have been discovered. The development of the chemical knowledge of the individual would then become an epitome of the actual historical development of the subject; and this knowledge would be far more easily grasped and assimilated than can possibly be the case when the subject is presented in any less natural way. It should, furthermore, be easy to see that the actual facts and relationships to be learned can be easier and better learned when they are kept free, at least at the beginning, of perverse statements which the stater himself does not try to prove. Clifford, who said many true things, never said a truer one than that no one should be asked to believe a thing until he is in position to appreciate the evidence for it. *J. E. Trevor*

Traité d' Analyse chimique quantitative par l' Électrolyse. *By J. Riban. 16 × 25 cm; pp. vi and 304. Paris: Masson et Cie, 1899. Price: paper 9 francs.* — The book is divided into four sections, the first devoted to general theory and apparatus, the second to the determination of single metals or metalloids by electrolysis, the third to the separation of the metals and the fourth to special technical problems. In the appendix there is a series of useful

tables though one regrets to see that the atomic weight of oxygen is taken as 15.96. The book is by far the best work that has appeared in French and could be recommended highly were it not for the fact that practically no references are given. Such recent work as that of Küster and v. Steinwehr is cited in the text and the author shows familiarity with the work that has been done in Germany and in America. This volume may be welcomed as another sign that the scientific isolation of France in chemical matters will soon be a question of the past. The historian of the future will record that physical chemistry in the hands of Raoult, Le Chatelier and Duhem has been the leaven.

Wilder D. Bancroft

The Spirit of Organic Chemistry. *By Arthur Lachman. 13 × 19 cm; pp. xviii and 229. New York: The Macmillan Company, 1899. Price: $1.50.* — This little volume consists of a series of sketches, each sketch showing the historical development of some problem or group of problems in organic chemistry. The subjects treated are: the constitution of rosaniline; Perkin's reaction; the constitution of benzene; the constitution of acetoacetic ether; the uric acids group; the constitution of the sugars; the isomerism of maleic and fumaric acids; the isomerism of the oximes; the constitution of the diazo compounds. This list shows that the subjects have been well chosen. The treatment is good, barring a misguided conscientiousness in splitting infinitives; and the volume is a very interesting one. There is a real need for books of this general type and it is to be hoped that it will not be long before we have a full-fledged literature of critical historical studies. Practically the only criticism that the reviewer has to make is that it would have been better to state more explicitly the facts which a hypothesis of multirotation must explain in order to be accepted. Incidentally, it would also be well to omit the inaccurate statement, p. 148: "Recent investigations show, however, that the molecular weight of the dissolved sugar in its initial and final conditions of rotation is one and the same, which fact precludes the addition hypothesis."

The author has given references copiously throughout the text; and has added both a subject and a name index, for which all readers will be grateful to him. There is also a six-page introduction by Freer.

Wilder D. Bancroft

Harper's Scientific Memoirs. *14 × 21 cm. New York: Harper and Brothers, 1899.* —

No. 1. The Free Expansion of Gases. By Gay-Lussac, Joule, and Joule and Thomson. Edited by J. S. Ames. 106 pp. Price: 75 cents.

No. 2. Prismatic and Diffraction Spectra. By Joseph von Fraunhofer. Edited by J. S. Ames. 68 pp. Price: 60 cents.

No. 3. Röntgen Rays. By Röntgen, Stokes, and J. J. Thomson. Edited by George F. Barker. 76 pp.

No. 4. The Modern Theory of Solution. By Pfeffer, van't Hoff, Arrhenius, and Raoult. Edited by H. C. Jones. 134 pp.

We greet with pleasure the beginning, in English, of a series of reprints and translations of classic scientific papers, analogous to Ostwald's justly valued *Klassiker* series. The general editor is Joseph S. Ames, of the Johns Hopkins

University, and he has secured the collaboration of a number of well known American men of science. Each of the little volumes is to contain a complete paper, or, in some cases, a collection of shorter papers, on some subject. Notes, explanations, and corrections are to be added when needed. In each case a synopsis of the present state of knowledge of the subject, together with a bibliography and an index, is to close the whole.

Four volumes are now out. The first, on the Free Expansion of Gases, contains the familiar papers by Gay-Lussac, Joule, and Thomson and Joule on this absorbing thermodynamic topic. Translation and editing have been done by the general editor. The second, likewise edited by Mr. Ames, gives a cycle of papers by Fraunhofer, on prismatic and diffraction spectra. The third, edited by George F. Barker, presents papers by Röntgen, Stokes, and J. J. Thomson, on the Röntgen rays; while the fourth is made up of a series of the memoirs of Pfeffer, van 't Hoff, Arrhenius, and Raoult, on the Modern Theory of Solutions.

This last volume is edited by Harry C. Jones. It is a most admirable one. It contains selected passages from Pfeffer's osmotic investigations, van' t Hoff's paper on the analogy between gases and solutions, Arrhenius's article developing the theory of electrolytic dissociation, and three papers by Raoult. It is a pity that one more paper had not been added: that of Raoult and Recoura, discussed by van 't Hoff, Zeit. phys. Chem. **5**, 423 (1890). Brief biographical sketches of Pfeffer, Arrhenius, van 't Hoff and Raoult have been supplied by the editor. This is an excellent idea; but in the case of Raoult, this has been carried out in such a way that the reader gets the impression that Raoult had never done anything of importance outside of his vapor-pressure studies. In the biography of van 't Hoff it is not clear why the work on active oxygen should not have been mentioned. These points are not of great importance, since the real value of the book consists in the translated papers; and this arrangement according to subjects is a very welcome one. In an appendix there is a partial bibliography of osmotic pressure, theory of solution, freezing-point and boiling-point methods. This does not claim to be complete, the editor intending to cite only the more important papers. Even after this reservation one does not quite understand how Naccari's work came to be omitted; and if Lord Kelvin's criticism of the osmotic pressure theory is to be cited, the answer by Gibbs should not have been ignored.

Very interesting further volumes of the series are announced as in preparation. Notable among these are numbers that are to treat the laws of gases, the second law of thermodynamics, electrolytic conduction, the law of gravitation, the Faraday and Zeeman effects, and the wave theory of light. *Editors*

Müller-Pouillet's Lehrbuch der Physik und Meteorologie. *By L. Pfaundler and O. Lummer. Vol. II, Part 2. 14.5 × 22.5 cm; pp. xiv and 768. Braunschweig: F. Viewig und Sohn, 1898. Price: paper 10 marks.*—Müller-Pouillet's well-known *Lehrbuch* is now appearing in its ninth edition. Of its different Parts, the one that contains most having a physicochemical interest is, naturally, the second part of Vol. II., on Heat. This portion of the work has been almost wholly rewritten; and much new material has thereby been incor-

porated in it, notably sections on the theory of solutions, and on the Gibbsian phase rule. It is, indeed, a gratifying indication of progress, to find eight pages devoted to the phase rule. The closing reference here to Meyerhoffer's little book might, however, have been replaced to advantage by a citation of Bancroft's far more comprehensive treatise on the same subject.

Thermometry, as a matter of course, introduces the present volume. This subject is followed by chapters on fusion and vaporization, calorimetry, thermochemistry, thermodynamics, kinetic theory, conduction and radiation, and meteorology. The whole work is primarily a treatise on experimental physics: theory appears in it only in so far as has apparently been deemed unavoidable. It is profusely illustrated by wood cuts, and is supplied with an index.

J. E. Trevor

Kurzer Abriss der Elektricität. *By L. Graetz. 16 × 23 cm; pp. vi and 180. Stuttgart: J. Engelhorn, 1897. Price: cloth 3 marks.* — The present little volume is a digest of Graetz's larger work on electricity, a book which has gone through many editions. It is a popular treatise, intended to give in simple form a coherent account of the more important electric phenomena, and of the views that are currently held in regard to them.

The most prominent peculiarities of the book are, perhaps, the order of treatment that is pursued in it, — the production and properties of electric currents being studied before electrostatic phenomena are taken up, — and a consistent attempt to represent all electric phenomena as changes in the state of the 'ether'. Concerning this latter point, the author remarks that although a wholly satisfactory ether theory does not exist, yet electric processes can be easily visualized as processes in the ether, and many of them, as for example electric oscillations, become thereby especially intelligible. Throughout the book, further, the presentation of scientific facts is always accompanied by an account of the more important technical applications that are made of them. The topics treated in the volume are, successively: the production of currents; the laws to which currents are subject; magnetic effects of currents; electrostatics; dynamos; the relations of currents to thermal, optic, and chemical processes; conduction by gases; electric waves. This is a comprehensive programme, and it is simply, clearly, and scientifically carried through.

J. E. Trevor

On the Study and Difficulties of Mathematics. *By Augustus De Morgan. New Edition. 14 × 20 cm; pp. vi and 288. Chicago: The Open Court Publishing Company, 1898.* — Of the instructive publications of the progressive Open Court Company, one of the most recent is an attractive reprint of De Morgan's little treatise on the Study and Difficulties of Mathematics. De Morgan issued the original work in 1831, and it has long been practically inaccessible. As a sensible and lucid commentary on the principles of arithmetic, algebra, geometry, and trigonometry, it cannot easily be surpassed. The author says that his object has been "to notice particularly several points in the principles of algebra and geometry, which have not obtained their due importance in our elementary works on these sciences." The way in which this has been done is ample justification for reproducing the work now. The editor of

the present edition, Mr. Thomas J. McCormack, says, very justly, that "De Morgan, though taking higher rank as an original inquirer than either Huxley or Tyndall, was the peer and lineal precursor of these great expositors of science, and he applied to his lifelong task an historical equipment and a psychological insight which have not yet borne their full educational fruit. And nowhere have these distinguished qualities been displayed to greater advantage than in the present work, which was conceived and written with the full natural freedom, and with all the fire, of youthful genius." *J. E. Trevor*

The Arithmetic of Chemistry. *By John Waddell. 12 × 18 cm; pp. viii and 133. New York: The Macmillan Company, 1899. Price: cloth, 90 cents.* — In the preface to this problem book, the author says: "The form that this book has taken is due to a very considerable experience of the difficulties encountered by students when attempting to make chemical calculations. The effort has been made to smooth away these difficulties, and to give an accurate, as well as a simple and systematic, treatment of the subject. A number of points are, I venture to think, more clearly presented than in other books; for instance, Charles's law and the so-called gramme-molecular volume of gases." The topics treated are: stoichiometric calculation of weights; calculation of the volumes of gases; calculations in volumetric analysis; and calculation of chemical formulas. Other matters, such as the metric system, comparison of thermometric scales, a table of combining weights, and a table of logarithms, are relegated to an appendix. All the calculations are clearly explained, and they are accompanied by a number of problems for practice. These problems have been taken from the examination papers of various British and American universities *J. E. Trevor*

The Metaphysic of Experience. *By Shadworth H. Hodgson. 14 × 21 cm. Vol. I. xx and 459 pp.; Vol. II. 403 pp.; Vol. III. 446 pp.; Vol. IV. 503 pp. New York: Longmans, Green and Co. Price: $12.00.* — Mr. Shadworth Hodgson, for fourteen years President of the Aristotelian Society, presents in four sumptuous volumes the results of the labor of eighteen years devoted to framing the outlines of a complete system of philosophy. His fundamental idea is that analysis of actual experience, avoiding assumptions, is the only trustworthy guide in developing a conception of the nature of the universe. It readily appears that all knowing is consciousness; but it does not follow from this that consciousness is the only existence of which we have evidence. From the experience that gives rise to the conception of real conditions possessing operative agency, it is concluded that there is an existence which is not consciousness, and which exists whether perceived or not. This existence, termed physical matter in contradistinction to percept-matter, constitutes the subject upon which consciousness, as an existent, is conditioned; it is the real condition of the arising of the special states of consciousness. And, finally, still from the analysis of experience, Mr. Hodgson is led to infer the existence of an unseen world, which forms, together with the seen world, an infinite universe adequately known in one ceaseless moment of awareness by an omniscient Percipient. The work thus ends in laying the foundation of a theology.

The text is divided into four books; of which the first contains the general

analysis of experience; the second a study of the connection between the positive sciences and philosophy; the third an analysis of conscious action, leading to establishment of the foundations of logic, aesthetics, and ethics; while the fourth has to do with the Real Universe. It cannot well be denied that Mr. Hodgson has produced here a notable work. *J. E. Trevor*

Annuaire pour l' an 1899, publié par le Bureau des Longitudes. *9 × 15 cm; pp. v and 658. Paris: Gauthier-Villars et Fils. Price: 1.50 francs.* — That reliable data book, the *Annuaire* of the *Bureau des Longitudes*, is now out for 1899. It contains the usual collection of astronomical, physical, and chemical data; and four appendices, the most important of which is an account, by M. Gautier, of the great siderostatic telescope he is building for the coming Exposition. The thing has an object-glass of nearly fifty inches (1.25 m) diameter, and a focal length of nearly 200 feet (60 meters). It is, thus, one quarter larger than the Yerkes glass. It is, however, to be fed by a huge mirror, which must occasion a great loss of light. *J. E. Trevor*

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry

General

On a possible change in weight in chemical reactions. *F. Sanford and L. Ray. Phys. Rev.* **7,** *236 (1898).* — Another attempt by the authors to corroborate Landolt's results (**2,** 137). This time they try the reduction of iodin from potassium iodid by means of ferric chlorid. The apparatus and method are the same as in their previous work, only greater care is taken with the weighings. From the results, extending over four months, a gain in weight rather than a loss is noticed. The gain recorded is 0.02 mg. *H. T. B.*

Note on the atomic weights of praseodidymium and neodidymium. *H. C. Jones. Zeit. anorg. Chem.* **19,** *399 (1899).* — Attention is called to the fact that the recent work of Scheele, of Brauner, and of Jones, point to the conclusion that in Auer v. Welsbach's original paper the molecular weights for praseodidymium and neodidymium were transposed. *W. D. B.*

A comparison of Rowland's thermometers with the Paris standard and a reduction of his value of the mechanical equivalent of heat to the hydrogen scale. *W. S. Day. Phys. Rev.* **6,** *193 (1898).* — Reviewed (**2,** 504) from Phil. Mag. [5] **44,** 169 (1897); **46,** 1 (1898).

Some modifications of the Geissler pump. *G. Guglielmo. Rend. Accad. Lincei, (5)* **7,** *II, 240 (1898).* — The author has made numerous changes, the most striking of which is the doing away with the long fall-tube. The new form of the pump may be purchased from Treffurth (Ilmenau) for twenty francs. *W. D. B.*

One-Component Systems

The vapor-pressures, specific volumes, and critical constants of normal heptane. *S. Young. Jour. Chem. Soc.* **73,** *675 (1898).* — Normal heptane boils at −3.4° under 9.2 mm and at 98.55° under 762.35 mm pressure. The critical temperature is 266.9° and the critical pressure 204.15 mm. The mean density of liquid and vapor is given very accurately by the formula $D_t = 0.3518 - 0.00044\,t$. The critical density is 0.2344 practically identical with those of isopentane 0.2344, normal pentane 0.2324, nornal hexane 0.2343. The ratio of the actual critical density to the theoretical critical density is 3.860. *W. D. B.*

On the density of ice. *E. L. Nichols. Phys. Rev.* **8,** *21 (1899).* — The author points out very justly the urgent need of a more careful study of the

density of ice. The occurrence of this constant in the use of the ice calorimeter renders it of considerable importance, and, as the summary of the work of previous observers shows, the divergences in the results are far from satisfactory. In the experiments here described the author studies the density both of natural and artificial ice by several well selected methods. A difference is found considerably beyond the errors of observation. This agrees with the most correct results of previous observers. For instance, the author's value for artificial ice is 0.91615, which agrees wonderfully well with the mean result of Plücker and Geissler, Bunsen and Kopp, i. e. 0.91614 for the same kind of ice. For natural ice the value found by the author is 0.91807, which also substantiates certain of the older results. The conclusions are then that natural ice is some 2 in 1000 denser than artificial ice. A very significant statement is also made, significant from the point of view of river ice formation in water flowing too rapidly to freeze over, that from certain preliminary results ice formed at $-5°$ to $-10°$ is less dense than that formed at $-70°$ by at least 1 in 1000. During extreme cold weather it is a well known fact that in northern rivers the rapidly formed fine ice particles in open water tend to float lower in the water than during milder weather. This possibly might be due to the denser state of the ice coupled with the fact that the water is very slightly undercooled which would render it less dense. *H. T. B.*

Kinetic theory of liquids. *C. Dieterici. Wied. Ann.* **66,** *826 (1898).* — A mathematical application to liquids of the ordinary equations relating to the kinetic theory of gases and a discussion of vapor pressures and heats of vaporization in that light constitute the main points of this paper. There is little new beyond a more complete treatment of the subject than has yet been given, and on the whole the paper is disappointing. The work of Clausius, van der Waals, Stefan, Jäger, Voigt and Milner are compared and extended. *H. T. B.*

The densities of liquids and saturated vapors as functions of the temperature. *C. Del Lungo. Rend. Accad. Lincei, (5)* **7,** *1, 353 (1898).* — Kinetic theory based on the assumptions that the velocity of the molecules of a liquid is equal to the velocity of the molecules of the vapor; that a liquid is a dense gas in which the crowded molecules are within the sphere of molecular cohesion; that the velocities of the molecules of a liquid are distributed among the molecules according to the same law as for vapors. *W. D. B.*

Piezometer for compressing and stretching liquids. *A. Pizzarello. Nuovo Cimento, (4)* **8,** *266 (1898).* — Two glass tubes are connected by a rubber tube. Mercury is poured in until one of the tubes is filled above a stopcock which is then closed. The other tube is then raised fairly rapidly and the mercury is said to follow making a vacuum in the closed tube, even though there is an apparent pressure of four atmospheres. This seems to be a most surprising experiment. *W. D. B.*

On the specific heats of gases. *Fourth Paper. Second Part. S. Lussana. Nuovo Cimento, (4)* **7,** *365 (1898).* — The specific heat of air C_p varies from 0.2931 at 39.53 atm to 0.4316 at 156.37 atm. (See **2,** 60.) *W. D. B.*

Two-Component Systems

The use of the transition temperatures of complex systems as fixed points in thermometry. *T. W. Richards and J. B. Churchill. Proc. Am. Acad.* **34,** *277; Zeit. phys. Chem.* **28,** *313 (1899).* — The authors give approximate transition temperatures for nine salts. They find for $Na_2CrO_4 10H_2O$, 19.93°; $Na_2SO_4 10H_2O$, 32.484°; $Na_2CO_3 10H_2O$, 35.2°; $Na_2S_2O_3 5H_2O$, 48.1°; $NaBr 2H_2O$, 50.8°; $MnCl_2 4H_2O$, 57.9°; $SrCl_2 6H_2O$, 61.1°; $Na_3PO_4 12H_2O$, 73.5°; $BaO_2H_2 8H_2O$, 78.0°. These are all temperatures on the mercury thermometer and are only first approximations subject to future revision, with the exception of the value for Glauber's salt (see **3,** 177). The authors propose 20° as standard room temperature, a suggestion which the reviewer approves most heartily. They point out that sodium chromate corresponds very closely to this value, 19.93° on the mercury scale, 19.85° on the hydrogen scale. *W. D. B.*

On the phenomena of physical equilibrium in mixtures of isomorphous substances. *G. Bruni. Rend. Accad. Lincei,* (5) **7,** *II, 138; Gazz. chim. Ital.* **28,** *II, 322 (1898).* — The author discusses Küster's hypothesis that the freezing-points of mixtures of isomorphous substances lie on the straight line between those of the two pure components, citing the experiments of Garelli made in 1894 to show that this is not true experimentally. From the phase rule he draws the sound conclusion that there is only one freezing-point curve, overlooking however that this is not incompatible with a maximum or minimum freezing-point for some mixture. He shows experimentally that mixtures of naphthalene and β-naphthol do not solidify without change of temperature and concludes finally that isomorphous mixtures are solid solutions. *W. D. B.*

New considerations on the physical equilibrium for isomorphous mixtures. *G. Bruni. Rend. Accad. Lincei,* (5) **7,** *II, 347 (1898).* — To prove that isomorphous mixtures cannot solidify without change of temperature the author quotes, nominally from Gibbs, a statement that "In a system containing two coexistent phases, it is necessary and sufficient that the two phases have the same composition for the temperature to be a maximum or a minimum at constant pressure." As a matter of fact the original passage, p. 155, reads: "for constant temperature the pressure is in general a maximum or a minimum when the composition of the two phases is identical. In like manner, the temperature of the two coexistent phases is in general a maximum or a minimum, for constant pressure, when the composition of the two phases is identical." The author's quotation is really from Duhem, Zeit. phys. Chem. **8,** 337 (1891) and he has overlooked the fact that a proof that the temperature can be a maximum or a minimum only when the composition of the two phases is identical does not necessarily prove the proposition that the two phases can be identical in composition only when the temperature is a maximum or a minimum. *W. D. B.*

Solubility of isomeric substances. *J. Walker and J. K. Wood. Jour. Chem. Soc.* **73,** *618 (1898).* — The authors have tested some of Carnelley and Thomson's generalizations with the following results:

1. The rule that the order of fusibility of isomeric substances is also the

order of their solubility does not hold good for the hydroxybenzoic acids. The rule is in general applicable to benzylcarbamid and its isomerides, the only exception found being benzyl- and paratolyl-carbamid in ether, where the solubilities lie close together, but not in the order of fusibility.

2. The rule that the order of solubility is independent of the solvent is subject to the same exceptions as the preceding rule.

3. The constancy of the solubility ratio observed by Carnelley and Thomson for meta- and paranitranilin is not found either with the hydroxybenzoic acids or with benzylcarbamid and its isomerides. The solubility ratio for any pair of the hydrobenzoic acids in the same solvent is also variable with the temperature.

4. The variation of the solubility of salicylic acid and its isomerides with the temperature can be expressed by a formula of the type proposed by Nordenskjöld, namely $\log S = aT - b$ when the solvent is water, but not when the solvent is benzene.

5. Congo-red was found to be the best acidimetric indicator for salicylic acid and its isomerides. The values obtained for the solubility of salicylic acid in water are only two-thirds of the values given by Bourgoin. *W. D. B.*

The freezing-point of water solutions of the sodium salt of mellitic acid. — *W. W. Taylor. Zeit. phys. Chem.* **27,** *361 (1898).* — The experiments were made to determine whether the molecular lowering of the freezing-point would approach the maximum value of 7×1.87 demanded by the dissociation theory. The apparatus used was Beckmann's with many of Abegg's refinements. With the most dilute solution a value of 5.92×1.87 was obtained. It was found in the course of preparing the salt that it crystallized with 17 molecules of water of crystallization instead of with 18 as it is given in Beilstein's *Handbuch*. More experiments are promised with salts of pyridin pentacarboxylic acid.

S. L. B.

Stannic bromid as solvent in cryoscopic determinations. *F. Garelli. Rend. Accad. Lincei (5)* **7,** *II, 27; Gazz. chim. Ital.* **28,** *II, 253 (1898).* — Experiments have been made with a sample of stannic bromid melting at 29.45°. The values of the constant were 247 with benzene; 245 with acetophenone; 278 with ethylene bromid; 276 with ethylene chlorid; 283 with bromoform; 277 with carbon tetrabromid; 310 with iodin; 285 with bromin. From these figures and the looks of the solutions the author decides that 280 is the most probable value. Assuming 7.16 cal for the heat of fusion of one gram of stannic chlorid, the constant should be 248. To come out with 280 the heat of fusion should be 6.48 cal.

It was expected that stannic chlorid and stannic iodid might form solid solutions with stannic bromid; but the values obtained for the reacting weights were 165 and 511 respectively instead of 259.9 and 625.5. On the other hand acetic acid and butyric acid gave values of 127.6 and 180 instead of 60 and 88.

W. D. B.

On the molecular weight of some inorganic salts. *N. Castoro. Gazz. chim. Ital.* **28,** *317 (1898).* — Mercuric chlorid, silver nitrate, cadmium chlorid, zinc chlorid and stannous chlorid give normal lowerings of the freezing-point when dissolved in methane. Cobalt chlorid and cupric chlorid give double the normal value while manganese chlorid gives 140 instead of 126. *W. D. B.*

On the cryoscopic behavior of the picrates. *G. Bruni and R. Carpenè. Gazz. chim. Ital.* **28,** *II, 71 (1898).*—Picric acid gives normal values in acetophenone. The authors have studied the behavior of eighteen picrates. Of these the picrates of naphthalene, phenanthrene, anthracene, α-naphthol, β-naphthol, phenylcumalin, α-naphthylamin, α-methylindole, α-β-dimethylindole, α-methyl-*p*-ethylindole, and carbazole gave half-normal values pointing to complete dissociation. The picrates of α-β-β-trimethylindolenin, α-β-β-trimethyl-α-methyleneindoline, α-β-β-trimethyl-α-methyleneindolin and α-methylgranatanin gave practically normal values while the picrates of α-methyldihydroïndole, β-β-diethyl-α-methylindolin and α-γ-dimethylquinolin gave values pointing to partial dissociation. *W. D. B.*

Enantiomorphism. *F. S. Kipping and W. J. Pope. Jour. Chem. Soc.* **73,** *606 (1898).* — The authors have made forty-six series of crystallizations of sodium chlorate from water and have counted the number of dextrorotatory and laevorotatory crystals. In only two cases were the numbers exactly equal; but the results varied on both sides of the mean in such a way that the most probable value of the number of dextrorotatory crystals per hundred is 50.08 ± 0.11. From solutions containing 200 g of dextrose to the liter in addition to the sodium chlorate about twice as many laevorotatory as dextrorotatory crystals separated. Adding mannitol to the aqueous solution increased the percentage of laevorotatory crystals while addition of isodulcitol had the opposite effect and dulcitol had no effect at all. *W. D. B.*

Specific gravities and boiling-points of mixtures of benzene and normal hexane. *D. H. Jackson and S. Young. Jour. Chem. Soc.* **73,** *922 (1898).* — Hexane boils at 68.95° under 760 mm pressure. Addition of seventeen percent of benzene raises the boiling-point less than 0.2°. The authors have determined the complete boiling-point curve for hexane and benzene. The results are tabulated as are also the data for the densities of different mixtures.

W. D. B.

On the vapor-pressure of crystallized hydrates whose vapor-pressure varies continuously with the composition. *G. Tammann. Zeit. phys. Chem.* **27,** *323 (1898).* — The author has determined the variation of the vapor-pressure with the percentage amount of water for eighteen natural silicates containing water of crystallization. All these cases proved to be solid solutions. (See **2,** 263.)

W. D. B.

The volatility of osmium as OsO_4 in a current of air or oxygen. *O. Sulc. Zeit. anorg. Chem.* **19,** *332 (1899).* — In an air-current powdered osmium volatilizes perceptibly as tetroxid at 212°, the reaction ceasing to be measurable at a little below this temperature. In a current of oxygen marked volatilization takes place at 170° while there is no reaction at about 155°. *W. D. B.*

On the expansion of solutions of ammonia salts, *II. U. Schiff and U. Monsacchi. Gazz. chim. Ital.* **28,** *I, 161 (1898).* — Reviewed (**2,** 201) from Zeit. phys. Chem. **24,** 513 (1897). See also **1,** 604.

Röntgen ray photography applied to alloys. *C. T. Heycock and F. H.*

Neville. Jour. Chem. Soc. **73,** *714 (1898).* — The authors have photographed sections of gold-sodium, gold-aluminum, copper-aluminum and silver-aluminum alloys; but do not draw any satisfactory conclusions from these observations. They have also overlooked the fact that the phases obtained by slow cooling are not necessarily the same as those obtained by rapid heating. *W. D. B.*

On the volumetric measurement of liquids and the preparation of normal solutions. *J. Wagner. Zeit. phys. Chem.* **28,** *193 (1899).* — Reviewed (**3,** 48) from the author's *Habilitationsschrift.*

Poly-Component Systems

A new fixed point for thermometers. Suggestion for a normal room temperature. *W. Meyerhoffer and A. P. Saunders. Zeit. phys Chem.* **27,** *367 (1898).* — The temperature of transformation of Glauber's salt, when sodium chlorid is present, is determined as 17.9°. The change occurs slowly and the temperature remains constant a long while. Both substances are cheap and readily obtained pure. This seems to be a convenient point at which to test thermometers. The suggestion is made that a universal normal room temperature be adopted to avoid the confusion arising from the lax use of the term "room temperature" which may mean anything varying between the limits of 6° or 8°. 17 9° may not be best for the purpose. Perhaps some other mixture will give a temperature nearer an even number of degrees. This notice is published in advance of the rest of an extended investigation because of the article by Richards and Churchill (Ibid. **26,** 690) on the same subject. *S. L. B.*

On the equilibria in systems with two and three components and one liquid phase. *G. Bruni. Rend. Accad. Lincei,* (*5*) **7,** *II, 198; Gazz. chim. Ital.* **28,** *II, 508 (1898).* — The author recapitulates the phase rule classification for such systems. *W. D B.*

Contributions to the chemistry of thorium: comparative researches on the oxalates of the rare earths. *B. Brauner. Jour. Chem. Soc.* **73,** *951 (1898).* — The double ammonium oxalate crystallizes with four and with seven of water and probably contains one of ammonium oxalate to one of thorium oxalate. It is decomposed by water with precipitation of thorium oxalate. The atomic weight of thorium was found to be 232.43, a value identical with that obtained by Krüss and Nilson. The author records some interesting quantitative measurements on the solubility of the rare earth oxalates in dilute sulfuric acid. *W. D. B.*

Theory of the mutual effects on the solubilities of two ion electrolytes when all the ions are different. *A. A. Noyes. Zeit. phys. Chem.* **27,** *267 (1898).* — If solutions of two electrolytes, AB and CD, each capable of dissociating into two ions, are mixed, and if all four ions are different, there will be eight substances in the resulting solution, the four ions, A, B, C, and D, the undissociated substances, AB, CD, and also AD and CB. The solubility of AB for instance is obviously greater than it would be in pure water. Considering the concentrations, solubilities, and degrees of dissociation of these substances, nine equations are obtained with nine unknown quantities, one of which is the new solubility

sought. The equation may then be solved, but the final equation would be extremely long and complicated. Such a general case is of small practical importance. In special cases much simpler equations may be derived. The author considers three such cases: First, where AD and CB are strongly dissociated substances. Second, where CD and AD (or CB) are strongly dissociated substances. Third, where AD (or CB) is a strongly dissociated substance. The mathematically correct formulas are still rather complicated, but by eliminating quantities which are small in comparison to others, an approximation to the true values is reached, and simple equations are obtained expressing the desired solubility as the only unknown. Solubility experiments are going on in the author's laboratory illustrating these three cases. He gives some of the results already obtained, and shows that the agreement between the values actually found and those calculated from his approximate equations, is highly satisfactory. *S. L. B.*

The solubility of salts of weak acids in stronger acids. *A. A. Noyes and D. Schwartz. Jour. Am. Chem. Soc.* **20,** *742 ; Zeit. phys. Chem.* **27,** *279* (*1898*). — An account of experiments on the solubility of silver benzoate in nitric and in monochloracetic acids of different concentrations. The chemicals were carefully purified and then analyzed to ascertain their purity. Saturation of the solutions was obtained by rotating the vessels containing them in a thermostat at 25°. At least eight hours were allowed for the solutions to become saturated. A definite volume was pipetted out and titrated with potassium rhodanate adding nitric acid and using iron alum as indicator. Each determination was made in two ways, once raising the temperature to 25° and once lowering it to the same point. The second method invariably gave higher solubilities than the first, but as repeated determinations by the first agreed much better than by the second, it is probable that the first method is the more accurate. In an attempt to make the results by both methods agree, the time allowed for saturation was lengthened to 72 hours without success. Tables are given of all the results, and these are also combined in other tables with results calculated according to the theory and equations of the preceding article and show excellent agreement. This is a fresh proof of the truth of the solubility principle and of the applicability of the theories of dissociation in the case of weak acids. *S. L. B.*

The solubility of iodine in dilute solutions of potassium iodide. *A. A. Noyes and J. Seidensticker. Zeit. phys. Chem.* **27,** *357* (*1898*) ; *Jour. Am. Chem. Soc.* **21,** *217* (*1899*). — It is highly probable from Jakowkin's work that iodin dissolving in potassium iodid forms the compound KI_3. If this is so then the equation $(KI_3) = k(KI) \times (I_2)$ must hold. The symbols represent the concentrations of the substances, and k is a constant. If the solution is always saturated with iodin, its concentration is a constant and the equation becomes $(KI_3) = k(KI)$. Careful experiments were made upon the solubility of iodin in potassium iodid solutions of concentrations varying between 0.1 and 0.005 normal, and in pure water. Subtracting the amount of iodin soluble in pure water from the total iodin in the various solutions, values are obtained for (KI_3). These values show the constant relation to the amount of KI present demanded by the equation. This furnishes a further argument in favor of Jakowkin's theory. *S. L. B.*

On the solubility of argentic bromide and chloride in solutions of sodic thiosulfate. *T. W. Richards and H. B. Faber. Am. Chem. Jour.* **21**, *167* (*1899*). — The solubility of silver bromid in sodium thiosulfate solutions at 35° increases somewhat more rapidly than the concentration of the sodium thiosulfate. Adding silver bromid to dilute solutions of sodium thiosulfate raised the freezing-point at first and further additions produced little or no effect. *W. D. B.*

On equilibrium phenomena in precipitates. *F. W. Küster. Zeit. anorg. Chem.* **19**, *81* (*1899*). — Equal quantities of a silver nitrate solution were added to solutions containing equal total amounts but varying relative amounts of potassium bromid and chlorid, chlorid always being present in excess. The precipitate was analyzed and the relative amount of silver bromid was found to vary continuously with the relative concentration of the potassium bromid in the solution. The same final equilibrium was reached even when silver nitrate was added to pure potassium chlorid solution and potassium bromid solution added after the precipitation. This disproves any hypothesis in regard to 'mechanical' occlusion and forces us to the conclusion that silver bromid dissolves in precipitated silver chlorid. It was found quantitatively that the distribution ratio for silver bromid remained surprisingly constant over a wide range of concentrations. *W. D. B.*

On red copper potassium chlorid. *M. Gröger. Zeit. anorg. Chem.* **19**, *328* (*1899*). — The author has obtained the well-known double salt $CuCl_2KCl$ by crystallization from a concentrated hydrochloric acid solution and has analyzed it. He reports that he had difficulty in getting the salt pure because it decomposed when he washed it. It is surprising that such an article should have passed the editors. *W. D. B.*

On the chemical equilibrium between amalgams and solutions. *A. Ogg. Zeit. phys. Chem.* **27**, *285* (*1898*). — Experiments testing the formula of Nernst (**1**, 605, 615). It was found that when mercury was shaken with silver nitrate solutions of not too great strengths the ratio of the concentrations of silver in the solution and the resulting amalgam was inversely proportional to the square root of the concentrations of mercury in the solution. This shows that the reaction taking place is

$$2Hg + 2\overset{+}{Ag} \rightleftharpoons \overset{++}{Hg_2} + 2Ag.$$

When a more concentrated silver nitrate solution is taken, a solid silver amalgam precipitates and the concentrations in the solution phase thereupon become constant. No satisfactory results were obtained when silver was shaken with mercurous nitrate. The composition of the solid silver amalgam was found to be Ag_3Hg_4 by the methods of Müller-Erzbach and of Andreae.

When mercury is shaken with a solution of mercuric nitrate the latter is reduced almost completely to mercurous nitrate. By determining the ratio of the two nitrates at equilibrium under different initial concentrations it is possible to deduce the form of the equation describing the reaction. It was found to be $Hg + \overset{++}{Hg} = \overset{++}{Hg_2}$, thus confirming the results with silver nitrate. The same result was obtained by measuring the electromotive force of a mercurous nitrate

cell, nitric acid being added to the two solutions to make the difference of potential between the two zero. In mercury, mercurous nitrate, silver nitrate, silver cells, silver is cathode when the nitrates are fifth-normal and anode when they are tenth-normal. The decomposition values for the mixed nitrates is lower than that of either pure metal. *W. D. B.*

Reversible zymohydrolysis. *A. C. Hill. Jour. Chem. Soc.* **73**, *634* (*1898*). — The author has studied the hydrolysis of maltose under the influence of maltase of yeast with special reference to the influence of the decomposition-products. It was found that the reaction was hindered by the presence of glucose and this hindering was due to the formation of maltose from glucose under the influence of the enzyme. The equilibrium is displaced toward the maltose and by increasing the total concentration. This is in the direction required by theory since one of maltose forms two of glucose and this dissociation should proceed less far, the more concentrated the solution. With an initial concentration of forty percent sugar in the aqueous solution about eighty-four percent of the maltose is converted into glucose. A few other values are given, and the change of the equilibrium with the concentration is that required by the theory, as is shown by the appended table made up by the reviewer. The values for the constant are calculated from the formula $KX^2 = (1 - X)V$, V being taken as unity for the forty percent solution.

Sugar concentration	Percentage of maltose hydrate hydrolyzed	K × 1000
2 percent	At least 99	2.0
4 "	" " 98	2.1
10 "	" " 91.5	2.5
20 "	" " 90.5	2.3
40 "	About 84	2.3

W. D. B.

On the determination of sulfuric acid in the presence of iron. *F. W. Küster and A. Thiel. Zeit. anorg. Chem.* **19**, *97* (*1899*). — Jannasch and Richards have proved that when barium sulfate is formed in presence of iron salts the occluded iron is carried down as ferric salt. Küster therefore drew the conclusion that if no iron were present as ferric iron, none would be occluded. He tested this hypothesis in two ways. First he precipitated his iron with ammonia, added barium chlorid before filtering and then dissolved the ferric hydroxid with hydrochloric acid. The precipitate contained no iron and had the right weight. In the second set of experiments the iron was converted into a complex salt by means of ammonium oxalate or tartrate, barium chlorid was added and the whole heated with hydrochloric acid. The result was eminently satisfactory. This is indeed a triumph as far as the iron goes; but one cannot help wondering whether some barium chlorid were not occluded. *W. D. B.*

On the determination of sulfuric acid in presence of iron. *G. Lunge. Zeit. anorg. Chem.* **19**, *454* (*1899*). — The author points out that his method of precipitating the iron with ammonia and filtering before determining the amount of sulfate takes no more time than the method of Küster and Thiel (preceding review). *W. D. B.*

Titration of persulfates. *M. LeBlanc and M. Eckhardt. Zeit. Elektrochemie*, **5**, *355* (*1899*).—The titration of persulfates with ferrous ammonium sulfate and permanganate is not satisfactory because the reaction between the persulfate and the ferrous salt takes place too slowly. Heating the solution to 70°–80° obviates the difficulty. *W. D. B.*

New studies on the formation of the red sulfid of mercury by the wet way. *U. Alvisi. Rend. Accad. Lincei*, (*5*) **7**, *II*, *97* (*1898*). — The author dissolved $Hg(C_2H_5S)_2$, $HgCl(C_2H_5S)$, $HgCl_2(C_2H_5)_2S$, HgCl in ordinary ammonium hydrosulfid solution and let the four solutions stand. A red precipitate of sulfid of mercury separated almost instantaneously from the first solution; from the second, third and fourth solutions there crystallized a black precipitate which then became red, the reaction running slowly in the third solution, and very slowly in the fourth. Ethyl sulfid was also formed. If hydrogen sulfid be passed into a boiling solution of ethyl mercaptid suspended in water, the color becomes red, then black, then red again. The red precipitate has the composition represented by the formula HgS, as in the preceding cases. *W. D. B.*

On silver bisulfid. *A. Hantzsch. Zeit. anorg. Chem.* **19**, *104* (*1899*).—When a solution of sulfur in carbon bisulfid is added to a solution of silver nitrate in benzonitrile, silver bisulfid, Ag_2S_2 is precipitated as a velvet-brown amorphous powder, from which carbon bisulfid dissolves no sulfur. If pyridin be taken as solvent, only the ordinary black sulfid precipitates. *W. D. B.*

Osmotic Pressure and Diffusion

The osmotic pressure of certain ether solutions and its relation to Boyle-van 't Hoff's law. *H. M. Goodwin and G. K. Burgess. Phys. Rev.* **7**, *171* (*1898*); *Zeit. phys. Chem.* **28**, *99* (*1899*). — Direct determination at 12.90° of the vapor-pressures of solutions of naphthalene, benzophenone and diphenylamin. From these data the osmotic pressures of the solutions were calculated (see **2**, 203) and compared with the theoretical values. In all three cases there were marked variations from the theory, the discrepancy being most marked in the most dilute solutions. The authors conclude that apparently each substance in solution has its own equation of condition connecting temperature, osmotic pressure and volume just as in the case of easily compressible gasses. [The more accurate the measurements the more important it becomes to determine whether the heat of dilution is really zero for each case. Where this is not true the formula of van 't Hoff does not apply.] *W. D. B.*

On the passage of solutes through copper ferrocyanid membranes. *A. Naccari. Nuovo Cimento*, (*4*) **8**, *260* (*1898*). — The author has experimented with sugar (342), salicin (280), mannit (182), paraldehyde (139), ethyl bromid (109), anilin (93), amyl alcohol (188), butyl alcohol (74), urea (58) and acetone (58). He states that the substances with the lower molecular weight pass the membrane while the others do not. This is only a preliminary note which is probably the reason why it is not stated where the dividing line comes. *W. D. B.*

Velocities

Study of reaction velocity with special reference to mixtures of aqueous alcohol. *W. Kistiakowsky. Zeit. phys. Chem.* **27**, *250* (*1898*). — This is an

extract from a paper published in Russian in 1896. The reaction studied was the ester formation, ethyl formate, both with and without addition of hydrochloric acid. By having both alcohol and water present in large excess relatively to the acid or the ester, the concentrations of the first two substances may be considered as constant and the reaction becomes a monomolecular reversible reaction with the acid and the ester as the two substances of varying composition. In order to get the two single reaction velocity constants the author splits the formula $(k + k_1) = \log\frac{\xi}{\xi - x}$ into $kt = \frac{\xi}{a}\log\frac{\xi}{\xi - x}$ and $k_1 t = \frac{a-\xi}{a}\log\frac{\xi}{\xi - x}$ where a is the initial concentration of the organic acid and ξ the equilibrium value. For the solutions containing hydrochloric acid, in which autocatalysis may be neglected, excellent constants are obtained in each series and a comparison of the different series shows that the constant is independent of the concentration of the alcohol provided this latter does not exceed seventy-five percent in grams. With no inorganic acid the phenomenon of autocatalysis occurs and the author contents himself with pointing out that the course of the reaction is qualitatively what it should be without attempting to deduce a formula which should represent the data. It is not surprising that this should have been omitted because, in one experiment, the reaction had only run about two-thirds of the way in six months. *W. D. B.*

On the rate of crystallization, II. *F. W. Küster. Zeit. phys. Chem.* **27,** *222 (1898).* — A continuation of the polemic with Tammann (see **1,** 619, 749; **2,** 448, 450). The rate of crystallization is defined as the rate at which a crystal growing in its supercooled melt pushes forward a surface into the liquid phase. This is identical with the reaction velocity observed experimentally only in case the advance of the solid takes place perpendicularly to the surface of the crystal. The author believes that this does not take place with less than five degrees supercooling but that it does for supercoolings varying from 5° to about 25°.

The author claims further that the experiments of Nernst and Abegg on the convergence temperature have shown that the crystallizing melt does not reach the freezing-temperature. He therefore rejects Tammann's hypothesis that the temperature in the surface of discontinuity is that of the melting-point.

W. D. B.

Mr. F. W. Küster's comments on the rate of crystallization. *G. Tammann. Zeit. phys. Chem.* **28,** *95 (1899).* — A reply to Küster (preceding review). The author presents the two alternatives: "Either we assume that the temperature at the surface of the crystals is that of the melting-point in which case the change of the rate of supercooling is to be explained in some other way or we may assume that the temperature of the surface of the crystals is lower than the melting-point and that this difference increases approximately proportionally to the supercooling in which case, judging from general experience, we should expect to have the rate of crystallization decrease with increasing supercooling. The author explains why he thinks that Küster is wrong in rejecting the first hypothesis.

To the reviewer this whole discussion seems like the crackling of thorns under a pot. To one who is outside the fray, it seems as though the temperature at the surface between the crystals and the melt were probably not that of the melting-point though the heat given out during freezing would tend to raise the temperature. If we eliminate this heat effect by conduction we shall then have two effects to consider. With increasing supercooling the liquid becomes more instable as shown by the increasing difference between the stable and metastable vapor-pressures. This factor, acting alone, would cause increasing reaction velocity with increasing supercooling. On the other hand all reactions run more slowly at lower temperatures. The final result is due to both these causes plus the evolution of heat as the melt solidifies. *W. D. B.*

Catalytic actions on the oxidation of hydriodic acid with bromic acid. *N. Schilow. Zeit. phys. Chem.* **27,** *513 (1898).* — The reaction $HBrO_3 + 6HI = HBr + 3H_2O + 3I_2$ is hastened or retarded by the presence of other substances. A definite mixture of solutions of potassium bromate and iodid and acetic acid was made up and portions were poured into test-tubes containing the substances to be investigated. The reaction went so slowly that the effects could be judged qualitatively by the change of color (iodin freed). A large number of inorganic acids and salts and organic substances were thus tested. The list is very long; no general conclusions were drawn from it. More substances hastened than slowed the reaction, many had no effect. The effects of potassium chromate and molybdate were measured quantitatively. Curves are given showing the course of the reaction with varying concentrations of the catalysor. Ostwald has shown that the acceleration may be defined as $1/t_x - 1/t_o$ where t_o is the time required to reach a certain stage of the reaction without the catalysor and t_x is the time required to reach the same stage with the catalysor. Using this formula, other curves are given showing the relation between the catalytic effect and the concentration of the catalysor. From these it is at once apparent that the relation is not a simple one. In the case of the molybdate it seems to be a logarithmic function. *S. L. B.*

The reaction between potassium permanganate and hydrochloric acid under the influence of catalytic agents. *J. Wagner. Zeit. phys. Chem.* **28,** *33 (1899).* — Reviewed (**3,** 48) from the author's *Habilitationsschrift.*

Electromotive Forces

Some electrochemical and thermochemical relations of zinc and cadmium amalgams. *T. W. Richards and G. N. Lewis. Proc. Am. Acad.* **34,** *87 (1898); Zeit. phys. Chem.* **28,** *1 (1899).* — The authors write the Helmholtz formula for electromotive force and heat effect in the form $\frac{dE}{E-h} = \frac{dT}{T}$ where $h = \frac{Q}{ne}$. If Q is not a temperature function, this integrates to $E = KT + h$ and differentiates to $\partial E/\partial T = K$. In other words the change of the electromotive force with the temperature is a constant provided the heat effect is not a temperature function.

For cadmium amalgam cells the observed values are one to three percent higher than the calculated values up to and including the nine percent solution.

The ratio of electromotive force to the absolute temperature remains practically constant up to the nine percent solution, having a value of about 0.000048 volt/degree. With a ten percent cadmium amalgam there were marked variations in the electromotive force and in the temperature ratio. Experiments with cadmium sulfate and cadmium iodid as electrolytes showed that the electromotive force was independent of the anion.

Measurements were also made with cadmium amalgam against metallic cadmium, and with zinc amalgam against metallic zinc. From these data the heats of amalgamation were calculated. For zinc a value of —2255 cal is obtained while Favre found —2100 cal by thermochemical measurements.

The authors point out that the potential of a saturated zinc amalgam differs by not more than a few thousandths of a volt from the value for pure zinc while a saturated cadmium amalgam may differ by a twentieth of a volt from that of the pure metal. They interpret this as showing the inaccuracy of the statement that "the potential of a saturated amalgam may be considered the potential of the pure metal." If they had worded their statement, as it should have been worded, that the potential of an amalgam saturated with respect to the metal may be considered the potential of the pure metal, the discrepancy would have disappeared and they would have drawn the conclusion, already established by the experiments of Mazotto and of Jager that the solid phase in a saturated cadmium amalgam is not pure cadmium.

Simply for the historical value it may be well to state that the paper by Cady (**2**, 551) though published practically simultaneously with this paper was completed subsequently to it. A comparison of the two papers shows clearly the harm done by the policy of isolation too prevalent in American Universities. Each paper would have been improved if the author had been familiar with the contents of the other. To cite merely one instance in each case, Cady's method of determining whether the heat effect was or was not a function of the temperature is distinctly inferior to that adopted by Richards and Lewis, while the latter have failed to recognize that their calculated values for the amalgam cells should be corrected for the temperature coefficient. *W. D. B.*

On the change of the free energy in molten halid compounds of some heavy metals. *V. Czepinski. Zeit. anorg. Chem.* **19**, *208* (*1899*). — The fused halids were electrolyzed for a few minutes between carbon electrodes and then the electromotive force of polarization determined. This gives approximately the value for a cell with a metallic and a halogen electrode, the salt being electrolyte. Measurements were made between 300° and 750°, the limiting temperatures varying with the fusibility, volatility and stability of each salt. With zinc chlorid the electromotive force dropped continuously from 1.576 volts at 408° to 1.21 volts at 728°. From these data a value of 94.51 cal is obtained for the heat of formation of zinc chlorid. With zinc bromid the electromotive force varies continuously from 1.349 volts at 340° to 0.853 volt at 670°; with lead chlorid from 1.271 volts at 466° to 1.022 at 786°; with lead bromid from 1.132 volts at 310° to 0.808 volt at 740°; with silver chlorid from 0.911 volt at 460° to 0.795 volt at 750°; with silver bromid from 0.813 volt at 440° to 0.492 volt at 730°; with silver iodid from 0.619 volt at 320° to 0.495 volt at 740°. In addition to these data the author calculates the heat of formation for each salt

and, in some cases, the heat of fusion of the metals. The electromotive forces are given to tenths of millivolts without comment; but it seems almost impossible that any of the values should readily be accurate to millivolts.

The author has also measured the cells Zn | $ZnCl_2$ | $PbCl_2$ | Pb and Zn | $ZnBr_2$ | $PbBr_2$ | Pb, everything being liquid. The values of the first cell remain practically constant at 0.25 ± 0.01 V, while the temperature changes from 367° to 688°. The values of the bromid cell are 0.229 V at 434° and are only about 0.038 V at 681°. If it were not for the volatility of the zinc bromid it was probable that a reversal of the current could be obtained. *W. D. B.*

On the change of the free energy in molten halid compounds of some heavy metals. *R. Lorenz. Zeit. anorg. Chem.* **19,** *283* (*1899*). — Commenting on the paper of Czepinski (preceding review) Lorenz points out that for a wide range of temperatures the difference between the electromotive forces of polarization for two metals is practically equal to the electromotive force of the Daniell combination for those metals. In other words $M_1 \mid M_1X \mid X \mid M_2X \mid M_2$ is practically equal to $M_1 \mid M_1H \mid M_2X \mid M_2$. This is discussed at length but not very successfully. It is pointed out that the most natural assumption would be that the potential difference between the solutions is zero; but if this is the case we must assume that the dissociation of zinc chlorid is equal to the dissociation of lead chlorid and that the dissociation of zinc bromid is equal to that of lead bromid, otherwise the potential difference $X \mid M_1X$ cannot be equal to that $X \mid M_2X$. This leads to the conclusion that the value of the chlorid cell must be equal to that of the bromid cell, which is not the case experimentally. Here the author has overlooked the possibility — made probable by the deductions of Luther — that the solution pressure of zinc in zinc chlorid is not the same as the solution pressure of zinc in zinc bromid.

It is pointed out that the heats of formation of the fused salts as calculated from Czepinski's data are practically constant over the whole range of temperatures. The author therefore applies the van 't Hoff formula for the change of the equilibrium with the temperature comparing the ratios of the equilibrium constants between two pairs of temperatures. *W. D. B.*

The contact-potential between metals and fused salts, and the dissociation of fused salts. *C. McC. Gordon. Proc. Am. Acad.* **34,** *59* (*1898*); *Zeit. phys. Chem.* **28,** *302* (*1898*). — The author has measured concentration cells consisting of two solutions of silver nitrate in potassium nitrate at the temperatures of 232° and 298°. In view of the fact that in aqueous solutions the transference number approaches 0.5 with rising temperature, the author feels justified in making the explicit assumption that the potential difference may be considered zero. In view of the conductivity of fused potassium nitrate it would seem as though this conclusion could stand even if the transference number for silver nitrate should be proved not to be 0.5. On the assumption of complete dissociation the electromotive force of such a cell can be calculated from Nernst's theory or assuming Nernst's theory the dissociation can be calculated from the electromotive force. With the solutions containing 0.1 percent and 1 percent silver nitrate the value found at 232° was 0.100 V, while the calculated value was 0.101 V; at 298° the found and calculated values were 0.110 V and

0.114 V respectively. The variation in the latter case is probably due to the fact that this cell did not remain constant, possibly owing to the direct action of silver on the nitrates at this temperature. The author determined the densities of the solutions and used volume concentrations in his calculations.

From measurements of the 0.1 percent solution against 50 percent and 100 percent silver nitrate solutions, the author calculates dissociations of 69 percent and 58 percent respectively. It appears to the reviewer that there has been made the tacit assumption that the solution pressure of silver in fused silver nitrate is the same as in fused potassium nitrate, an assumption that is rendered improbable by the theoretical treatment of Luther. It is quite possible, however, that the correction to be applied is small in this particular case.

W. D. B.

Electrodes of the third class. *R. Luther. Zeit. phys. Chem.* **27,** *364 (1898).* — By having two solid phases it was possible to make an electrode that may be considered as reversible with respect to a metal of the alkalies or of the alkaline earths. A lead electrode dipping into a solution of calcium chlorid saturated with respect to lead and calcium sulfates is an instance of this type. The product of lead as ion and sulfate as ion is constant owing to the presence of solid lead sulfate. The product of calcium as ion and sulfate as ion is constant owing to the presence of solid calcium sulfate. Therefore the ratio of lead as ion to calcium as ion is constant, and if we may ignore the concentration of calcium sulfate with reference to the concentration of calcium chlorid the concentration of lead as ion will vary directly and the electromotive force will vary inversely as the concentration of dissociated calcium chlorid.

W. D. B.

On concentration cells with indifferent electrodes. *K. Schaum. Zeit. Elektrochemie,* **5,** *316 (1899).* — If an oxidation reduction cell be made up in which the oxidizing agent changes into the reducing agent and vice-versa, the total heat effect is zero and the electromotive force must therefore be proportional to the absolute temperature. Such a cell would be a dilute and a concentrated solution of mercuric chlorid with platinum covered with mercurous chlorid as electrodes. *W. D. B.*

Behavior of the polarization in electrolytes from ordinary pressure up to about one thousand atmospheres. *R. Frederico. Nuovo Cimento, (4)* **8,** *145, 409 (1898).* — The electrodes were of platinum, not platinized, 230 × 8 mm. The electromotive force of polarization for 8 percent sulfuric acid as measured increased from 1.911 volts at one atmosphere to 2.024 volts at 987 Atm; for 10 percent nitric acid the values are 1.752 at 1 Atm and 1.787 at 970 Atm; for 10 percent hydrochloric acid 1.313 at 1 Atm and 1.351 at 995 Atm. *W. D. B.*

Relations between the solubility and heat of formation of electrolytes. *G. Bodländer. Zeit. phys. Chem.* **27,** *55 (1898).* — Next to nothing is known as to a connection between the solubility and other properties of a substance. Nernst has shown that a limit to the solubility of an electrolyte may be calculated from the potential requisite to separate the ions out of solution. For example, if a normal solution of silver iodid could be obtained it would break

down into silver and iodin with a development of 0.26 volt. Therefore so strong a solution cannot exist. The author's purpose is to demonstrate that the solubility may be accurately calculated if, besides the potential requisite for the separation of the ions out of the solution into an electrically neutral state, account is taken of the potential involved in the separation of the solid substance into its ions. If a saturated solution of an electrolyte containing an excess of the solid, is electrolyzed, the concentration of the solution does not alter, and the process is simply one of separating the solid substance into two components. The potential required is then a measure of the firmness with which the products of the electrolysis are held together in the solid. Use is made of Nernst's formula for determining the potential necessary to electrolyze a substance from the pressures of solution and the concentrations of the ions in the solution, and of Thomson's rule that the heat of formation of a compound is proportional to the potential necessary to disintegrate it, and a formula is derived expressing the solubility in terms of potential and heat of formation. The derivation cannot be given in a review, but the formula resulting is, $0.116\ (0.087,\ 0.058) \log p = E_a + E_\kappa - \frac{Q}{230}$, where E_a and E_κ are the potentials needed to separate out anion and cation respectively, Q is the heat of formation of the compound and p is the concentration of the ions in solution. The number by which $\log p$ must be multiplied depends upon the valence of the ions in question. The values for E_a and E_κ being known and also the value of Q for the salt, the solubility is calculated and compared with the solubility actually found. The author did not carry out any experiments and confines himself to data furnished by others, tabulating the results of his calculations and of experiment side by side. The agreement is by no means complete, but it may be said that although different pairs of values are widely apart in absolute size, the values which should be the same are without exception of the same magnitude. Some apparent exceptions are explainable by the abnormal behavior of certain substances in solution. For example, cadmium iodid does not give cadmium and iodin ions, but probably forms complex ions such as CdI_4. Again in the case of substances such as bromin and chlorin the heats of liquefaction and vaporization must be brought into the calculation and prevent plain sailing. Other special details must be considered in other cases. When this has been done, even these exceptions show an approximate agreement between the results of calculation and of experiment, so the author feels justified in his theory by the facts.

The results are summed up in two rules applicable to electrolytes of small solubility. (1) "The greater the tendency of the acid radical to go from the electrically neutral state into the state of ions, the greater is the solubility of salts of one and the same metal with that acid." (2) "The greater the tendency of the metal to go from the electrically neutral state into the state of ions, the greater is the solubility of salts of one and the same acid with that metal." The difficultly soluble halogen salts furnish an example of the first rule; iodin having the least tendency to form ions, the iodids are the least soluble. Further, sulfids are less soluble than the difficultly soluble halogen salts, conforming to the yet smaller tendency of sulfur to ionize. The series of the

sulfids serve as an example of the second rule. Metals which decompose water, so great is their tendency to go into the state of ions, form soluble sulfids. Metals which generate hydrogen only from acids, as iron and zinc, form sulfids little soluble in water but soluble in acids. The other metals from copper to gold have so slight a tendency to ionize that their sulfids are soluble only in nitric acid or aqua regia. It is not new and original with the author however, that the order in which metals arrange themselves according to their potentials in contact with solutions containing their ions, is both the order in which they are precipitated by a gradually increasing electromotive force, and the order in which their sulfids are precipitated by hydrogen sulfid.

By a rearrangement of the formula it is shown how, from the heats of formation of salts and the potentials required to electrolyze them, it may be calculated which salt of the same base with two acids, or of the same acid with two bases, is the more soluble. This is of especial interest in the case of the halogens, as it offers a plausible explanation of the fact that the order of solubilities of the difficultly soluble halogen salts is exactly reversed for the readily soluble salts. Fluorin has been considered as abnormal and not thoroughly fitting in the series of halogens because silver fluorid is soluble and the other silver salts are commonly spoken of as insoluble. It is shown that the solubility of the silver salts increases rapidly (about 1300 times) from the iodid to the chlorid, and so the further increase in passing to the fluorid, so far from establishing an exception, is but a remarkably good example of the regular change of a given property from one member to the next of the halogen group.

S. L. B.

The electromagnetic effect of electrolytic current. *S. Sheldon and G. M. Downing. Phys. Rev.* **7,** *124 (1898).* — The authors endeavor to obtain by the usual ballistic method the magnetic effect of electrolytic currents. Their method is to replace the primary coil on a closed iron ring by a suitable length of rubber tube containing sulfuric acid of maximum conductivity which would give the same number of ampere turns. It was impossible for them to detect any difference between the current as conducted through copper wire or through the electrolyte. They discuss their results from two points of view, that of electrolytic conduction as we understand it to be due to the travelling of oppositely charged ions and that of metallic conduction which they think cannot be due to this but to some possible etheric stress. Their results throw no light whatever upon the complex question of the nature of conduction, indeed they are what we would expect regardless of any assumption as to how the electricity was conveyed. There is moreover a tendency now to regard metallic conduction from the ionic standpoint. Whether this is so or not must be shown by further experiment.

H. T. B.

On the fall of potential at the surface of a metal when exposed to the discharging action of the X-rays. *C. D. Child. Phys. Rev.* **6,** *285 (1898).* — Reviewed (**3,** 60) from Wied. Ann. **65,** 152 (1898).

On a new accumulator. *H. Bornträger. Zeit. Elektrochemie,* **5,** *324 (1899).* — A very effective accumulator plate may be made by pressing a mixture of spongy lead and lead peroxid into a lead lattice-work. The pressure is

about 100 Atm on the frame and 5-10 Atm on the intervening spaces. Attention is also called to the advantages of spongy lead and of lead peroxid as reducing and oxidizing agents. *W. D. B.*

On the removal of lead sulfate and the working up of lead residues in accumulator factories. *H. Bornträger. Zeit. Elektrochemie*, **5**, *325* (*1899*).— According to the author the only satisfactory way of cleaning accumulator plates is to fasten each to two zinc plates and let the whole stand twenty-four hours or less in twenty-five percent hydrochloric acid. To work up lead residues add twenty-five percent hydrochloric acid, heavy zinc plates and shake occasionally. The products are metallic lead, zinc chlorid and zinc sulfate. By adding barium chlorid to the solution, one gets dissolved zinc chlorid, which can be used for preserving wood, and precipitated barium sulfate. *W. D. B.*

A new interrupter for laboratories. *F. Dessauer. Zeit. Elektrochemie*, **5**, *357* (*1899*). — The vibrating spring makes two contacts, cutting out the electromagnet at the end of each swing instead of at the end of each double vibration. The contact is made half way down the spring instead of at the end. The principle seems an excellent one, as the spring need only vibrate one-half as fast as in the ordinary instrument. *W. D. B.*

On a new form of capillary electrometer. *G. Vanni. Nuovo Cimento*, (*4*) **7**, *393* (*1898*). — Reviewed (**2**, 515) from Rend. Accad. Lincei, (5) **7**, I, 309 (1898).

Electrolysis and Electrolytic Dissociation

A new determination of the electrochemical equivalent of silver. *G. W. Patterson, Jr., and K. E. Guthe. Phys. Rev.* **7**, *257* (*1898*).—The present paper is a record of a series of experiments made by the authors to determine the electrochemical equivalent of silver and to obtain also an absolute measurement of the Clark cell. As a current-measuring instrument they use a type of British Association electrodynamometer designed by themselves. Their method briefly consists in balancing the force between the suspended and fixed coils by means of the moment of torsion of a phosphor-bronze suspension. The current through the dynamometer also passes through a known resistance. The difference of potential in the resistance is compared with two Carhart Clark cells on a suitable potentiometer. Two silver voltameters can also be included in the circuit. Their final value for the electrochemical equivalent of silver is 0.011192. This is almost exactly 1 in 1000 larger than Lord Rayleigh's and the later determinations of Kahle.

The observations given by the authors agree very fairly well and altogether the work seems carefully done, except perhaps the use of pine wood in the construction of the fixed coil of the dynamometer. As the dimensions of this coil are of such fundamental importance it would have been better to use some material that would not have shrunk so. At present no direct measurements are given for the E.M.F. of the Clark cell, but the work is to be continued with a view to studying this most important value. *H. T. B.*

Determination of migration velocities by electrolysis of dilute salt solutions. *W. Bein. Zeit. phys. Chem.* **27**, *1* (*1898*). — The author points out that since

1859 when Hittorf published his results there have been no systematic investigations of the velocities of migration of the ions, in spite of the need of accurate measurements of these values. Owing to the vastness of the subject he confines his measurements to a few more important salts and a study of sources of error in such measurements. Errors may be caused by reactions at the electrodes, by membranes in the solution, by diffusion, by electrical spreading through the solution of a product of the electrolysis and by the nature of the solvent. A lengthy chapter is devoted to a consideration of this spreading of one of the products of electrolysis and a very complete review is given of work that has been done on this subject. Where one of the ions is colored, or may be made visible by means of a suitable indicator, the rate at which the color progresses through the liquid has been used by a number of investigators to determine the velocity of migration. The author concludes that this method leads to accurate results only under certain definite circumstances. A number of color changes are mentioned which lend themselves well to qualitative experimental demonstrations of the movements of ions in solutions. The apparatus used is carefully described and illustrated with cuts. The anode and cathode were in separate vessels connected by tubes of varying lengths. No membranes were used. In some instances the length of the connecting tube was 50 cm. The high resistance was no great obstacle, as a potential of 110 volts was employed. During an experiment the whole apparatus was in a large water-bath. Tubes in this allowed the vapor of some boiling liquid as acetone, ethyl alcohol or water to be used for heating. The temperature was constant within 1 to 2 degrees and was varied in different experiments from 0° to about 97°. At the end of the experiment connection was broken between the two vessels by a stopcock, or by a pinch-cock on a bit of rubber tube, or by raising the level of a body of mercury causing some to flow in and divide the solution. The anode or the cathode solution or both were analyzed for the results. It is found that a cadmium anode absorbed some chlorine, probably precipitated as a basic salt during the electrolysis, although no change was apparent in the appearance of the anode. A correction had to be made for this or no accurate results could have been obtained. Experiments were carried out with fifteen different chlorids, a few iodids and bromids, some sulfates, nitrates and carbonates, acids and alkalies. A few of the more interesting results were as follows: Contrary to Hittorf's observations, no change was found in the rate of migration with the concentration, in a range of 1/5–1/200 normal HCl. In the case of NaCl also the rate of migration was unchanged for a range of concentration from 1/3–1/200 normal. In the case of HCl an increase of temperature increased the rate of migration; in the case of NaCl it diminished it. In the cases of KCl and LiCl temperature seemed to have no effect. The results with acetate of silver were different and higher than those obtained by Nernst and Hittorf. The results with sulfuric acid differed widely from Hittorf's. But it is not possible to do justice to such a wealth of experimental data in a short review, and one interested in the subject must read the original. *S. L. B.*

Electrolytic reduction of *m*-nitrotoluene. *A. Rohde. Zeit. Elektrochemie*, **5**, *322* (*1899*). — To make *m*-azotoluene start with 10 g *m*-nitrotoluene, 1 g sodium acetate and 250 cc of 70 percent alcohol. Pass in 7.9 ampere-hours

making the current density $D_{100} = 7$–8 amp. The yield is ninety percent of the theoretical. To make *m*-hydrazotoluene pass in ten ampere-hours, keeping everything else the same. To prevent oxidation, cool and add water until no more oil separates, then break the circuit. The author did not succeed in getting the *m*-hydrazotoluene to crystallize, though he believes that it can be done.

W. D. B.

On the electrolytic conductivity of pure substances. *R. Abegg. Zeit. Elektrochemie*, **5**, *353* (*1899*). — Judging from experience three essential factors for the conductivity of pure substances are a high dielectric constant, no polymerization, and components which can assume electric charges. These three requisites are present in fused salts. The associating effect of a solvent is evidently increased by a high dielectric constant and marked polymerization; but it is clear that other factors have to be taken into account. *W. D. B.*

On conduction in mixed salt solutions. *H. Hoffmeister. Zeit. phys. Chem.* **27**, *345* (*1898*). — The amount N of any univalent ion which passes through a given cross-section in unit time under the influence of a definite current is given by the formula: $N = UeC\frac{I}{\lambda}$, where U is the velocity of the ion, C its concentration, e the electrostatic charge, I the strength of the current, and λ the conductivity of the solution. Since N can be measured analytically this equation can be used as a means of determining C. This equation has been applied to mixtures of silver nitrate and nitric acid and of sodium acetate and acetic acid. With silver nitrate and nitric acid it was found that when either was present in excess, the dissociation of the other was forced back; but that there was little relative change when neither electrolyte was present in excess. With sodium acetate and acetic acid it was found that the acetic acid practically took no part in the conduction, the dissociation having been forced back so completely by the sodium acetate. *W. D. B.*

Comment on the preceding paper of Herr Hoffmeister. *H. Jahn. Zeit. phys. Chem.* **27**, *354* (*1898*). — It is pointed out that λ_v/λ_∞ is a measure of the dissociation only in case the migration velocities are independent of the concentration. [This is never the case when the transference number is a function of the concentration and is not necessarily so even when the transference number is a constant.] The author considers that the cause of a variation in the migration velocities of the ions is to be found in the mutual action of the electrostatic charges of the ions and, for this reason, he considers that no improvements in methods of measuring conductivity can ever enable us to verify Ostwald's dilution law for strong electrolytes. *W. D. B.*

Experiment on electrolytic conductivity without electrodes. *H. Behn. Zeit. Elektrochemie*, **5**, *402* (*1899*). — The author has measured the currents induced in a closed ring containing an electrolytic solution by the oscillating magnetic field of a transformer. No reference is made to Boys and Guthrie.

W. D. B.

ELECTROLYTIC DISSOCIATION AND TOXIC EFFECT

BY J. F. CLARK

I. INTRODUCTORY

The object the writer had in view in undertaking the investigation, the results of which are presented in this paper, was to determine approximately the relative and absolute toxic properties of a few deleterious agents as shown by their influence on the spores, the mycelium, and the fructification of certain of the mold fungi.

In recent years the study of plant pathology has come to be one of the most important in the whole range of botanical research. It seems desirable, therefore, that all possible light should be thrown on the toxic properties of the various agents used in combating fungous pests. It is also very desirable from a scientific point of view, to throw all light possible on the problem as to the *element* or *group of elements* to the influence of which the toxic properties of the compound are to be attributed.

It has been the aim of the writer to supplement the excellent work of Drs. Kahlenberg, True,[1] and Heald[2] on phanerogams and Drs. Krönig and Paul[3] on bacteria by applying the theory of the electrolytic dissociation of the molecule to the study of the physiology of the effect of toxic agents on the mold fungi.

II. METHODS

1. *Selection of Forms.* — In selecting forms the following points were given particular consideration: (a) *regularity of germination*, (b) ability to grow *normally* in a liquid medium, (c) ability to fruit normally in a saturated atmosphere. After

[1] Bot. Gaz. **22**, 81 (1896).
[2] Ibid. **22**, 125 (1896).
[3] Zeit. f. Hygiene u. Infect. **25**, 1 (1897).

experimentation with a large number of forms the following were chosen as being very well suited for the work : *Aspergillus flavus* Link, *Sterigmatocystis nigra* v. Tieghem, *Œdocephalum albidum* Saccardo, and *Penicillium glaucum* Link. *Botrytis vulgaris* Fr. was afterwards chosen as a fifth form, it being entirely satisfactory in regard to germination and mycelial development and especially desirable on account of its semi-parasitic habit. It, however, failed to fruit in cell cultures. Pure cultures of these fungi were obtained and renewed from week to week. The spores used in inoculating the cultures in the experimental work were taken from fresh tubes in which the fungus had been growing seven to fourteen days. A solid medium made by adding twelve grams of agar to a liter of sugar beet infusion was found to be very satisfactory for stock cultures.

2. *Selection of Medium.* — The object being to test the effect of the deleterious agents on the fungi when growing in as nearly normal conditions as possible, the selection of a suitable medium became a very important matter. Many preliminary cultures were made with various media, including distilled water, infusions of potato, celery, sugar beet, prune, and bean (stems, pods, and mature seeds), besides various others compounded from inorganic salts, sugars, asparagin, etc. The results in germination and development were very varied. In distilled water *Sterigmatocystis* and *Penicillium* failed to germinate in 24 hours and none of the five forms germinated more than 40 percent. Mycelial development was meager, and fruiting generally *nil*. Very minute quantities of the deleterious agents were found to inhibit germination, but the *death-point* of the spore was found, in the case of dichloracetic acid, potassium hydroxide, and cobaltous sulphate, to be the same in pure water as in the medium finally selected. The media compounded from salts, sugars, etc., were more satisfactory ; the vegetable infusions, however, were superior to all others. An infusion of the sugar beet was ultimately chosen and used throughout the work. It was made by steeping 450 grams of the root, sliced thin, in a liter of water for three hours at 100° C. After strain-

ing and cooling, the whites of several eggs were added and it was again boiled, then strained, filtered, and poured into flasks. After thorough sterilization the infusion was ready for use. In order to get the greatest possible uniformity it was found desirable to make up four or five liters at a time. In this medium the spores of the forms selected germinated in from 3 to 8 hours and with great uniformity, grew rapidly, and fruited normally (except *Botrytis*) in from 18 to 48 hours at a temperature of 28° C.

3. *Method of Culture.* — The van Tieghem hanging-drop culture was found to be entirely satisfactory. The cylinder part, which was of glass, had an internal diameter of 17.5 mm and was 10.7 mm in height. This provided an abundance of oxygen for the normal development of the fungi. The cylinders were cemented to the slip by means of beeswax, and the covers were sealed to the cell by means of a ring of vaseline applied to the top of the cell by inverting it on a glass slip covered by a thin layer of melted vaseline. A small nick was made in this ring so that when the cover was applied a minute opening might be left through which the expanding air could pass when the cultures were placed in the thermostat at 28° C. An hour later they were carefully examined and such as had not already become hermetically sealed were now made so by tapping with a pencil over the tiny opening referred to above. This precaution prevents much trouble and loss when culturing with volatile substances. For convenience in handling and examining under the microscope two cells were placed on each slip. The cells were permanently labeled by gumming lettered and numbered labels to the ends of the slips. As a precaution against accidents duplicate cultures were never placed on the same slip.

The various dilutions in beet infusion of the compound to be tested were made up in a dozen or more bottles of about 30 cc capacity. Each bottle was provided with a glass rod, drawn to a blunt point, by means of which the culture drop was transferred to a cover. *Four or five drops of the same solution were then placed in the bottom of the cell.* The spores of the fungus

to be tested were transferred from a pure culture to the hanging-drop by means of a sterile platinum needle, the utmost care being taken to *prevent the adherence of the spores in bunches* in making the inoculation. The cover bearing the culture was then inverted on the cell and gently pressed until completely closed except for the minute opening already fully described. When a set of cultures was complete all were placed in a thermostat which was kept at a constant temperature of 28° C.

4. *Care of Cells, Covers, Pipettes, etc.* — After the completion of a series of cultures all bottles, rods, etc. were thoroughly washed and placed in running water for several hours, then dried and placed in a dry oven at 160° C. When the cultures in the cells matured, the covers were removed and the cells were thoroughly washed under the water tap, wiped, air-dried, and finally placed in a dry oven at from 110°–120° C for an hour. This gave thorough sterilization, and at the same time drove off the last trace of any volatile substance which might have escaped the washing. The covers were first boiled in strong KOH, then in several changes of water. This was followed by boiling in strong $H_2SO_4 + K_2Cr_2O_7$, they were then thoroughly rinsed, and again boiled in four changes of clear water, rinsed in 95 per-cent alcohol, wiped, and sterilized at 160° C. The pipettes were cleaned by forcing water through them for an hour by attaching to a water tap. They were then sterilized in a steam sterilizer.

An occasional culture was found to be contaminated by bacteria, due no doubt to dust particles bearing spores coming in contact with the culture in the making. Such contamination, however, by bacteria or fungi amounted to less than one per-cent of the cultures made up after completion of preliminary experimentation.

5. *Vapor Pressures in the Cell.*— It has long been known to physical chemists that every liquid has a certain *vapor pressure.* Previous experimenters, testing the toxic properties of aqueous solutions of various substances by means of the hanging-drop culture, have, strange to say, overlooked this very important matter. This fundamental error led to much difficulty in manipulation and caused exceedingly erratic results. The diffi-

culties of making hanging-drop cultures containing, say, 10 per-cent alcohol or potassium hydroxide when there is a drop of *water* in the bottom of the cell, will be very evident to the reader. The very erratic character of the results to be expected is well shown by a test of spores of *Macrosporium* in solutions of mercuric chloride.[1] In a solution of $n/819200$ $HgCl_2$, three cultures grew and one failed; of eight cultures in $n/409600$, five grew and three failed; of ten cultures in $n/204800$, four grew and six failed; of four cultures in $n/102400$, one grew and three failed. This irregularity of germination was doubtless due to two factors, viz. variations in the size of the hanging-drops and variations in the quantity of water below. Were it possible to have all hanging-drops of *exactly* the same size, and exactly the same quantity of water in the bottom of the cells we should get *uniformity* in results. Such uniformity, however, would be useless, perhaps worse than useless, in that it would tend to prevent attention being called to the fundamental error of the method, viz. the use of solutions of varying vapor pressures in the same cell. A strictly non-volatile or less poisonous substance would, necessarily, show somewhat less variation than that shown by mercuric chloride quoted above. The less difference there is between the vapor-pressure of the mixture in the hanging-drop and that of the water below, the slower will the error be in manifesting itself by its effect on germinations. Of the volatile properties of $HgCl_2$ we shall have more to say later.

In looking for a method that would meet every requirement of the case, many preliminary tests were made with all five forms of molds used and with different deleterious agents. Two such tests with potassium cyanide are here presented in detail. It is of interest to note that while KCN is not in itself a volatile compound, in aqueous solution more or less hydrolysis takes place, resulting in the formation of a corresponding amount of the deadly HCN,[2] which is quite volatile. Hence aqueous solutions of KCN are in their behavior quite typical of solutions of volatile compounds.

[1] F. L. Stevens. Bot. Gaz. **26**, 377 (1898).

[2] Shields. Zeit. phys. Chem. **12**, 167 (1893).

Aspergillus IN BEET INFUSION + KCN

Temperature 28° C.

Culture label	Strength of solution	Conditions in cell	Germination 12 hrs pct	Germination 24 hrs pct	Germination 36 hrs pct	Development 12 hrs μ	Development 24 hrs μ	Development 36 hrs μ	Notes
A1	— KCN	(Check culture)	100			250	∞	∞	Fruited in 20 hrs.
A7	$\frac{n}{32}$	Dry	25	100		barely germ	45	200	
A7	"	"	10	100		"	40	100	
A8	"	One drop of water	7	100		"	120	500	
A8	"	"	5	100		"	100	800	
A9	"	Cell half filled with water	45	100		140	∞	∞	Fruited well at 38 hrs.
A9	"	"	70	100		150	∞	∞	"
A10	$\frac{n}{128}$	$\frac{n}{128}$ KCN solution below	0	0	75	—	—	100	
A10	"	"	0	0	10	—	—	80	

Penicillium IN BEET INFUSION + KCN.

Temperature 28° C.

			pct	pct	pct	μ	μ	μ	
E1	—KCN	(Check culture)	100			110			Well fruited at 24 hrs.
E7	$\frac{n}{32}$	Dry	0	5	10	—	barely germ	no growth	
E7	"	"	0	3	10	—	"	70	
E8	"	One drop of water	.1	10	25	barely germ	20	150	
E8	"	"	.01	10	20	"	20	130	
E9	"	Cell half filled with water	2	70		8	80	∞	Fruited at 36 hours.
E9	"	"	10	75		15	100	∞	"
E10	$\frac{n}{64}$	$\frac{n}{64}$ KCN solution below	0	0	0	—	—	—	
E10	"	"	0	0	0	—	—	—	

Explanatory—Column 1 gives the culture label by means of which the cultures were identified; column 2 the concentrations of KCN in the hanging-drops of the various cultures. Column 3 gives the solution — if any — used in the bottom of the cell. "Dry" implies that no water or other solution was placed in the bottom of the cell. Under the head "germination" the percentage of spores germinated is given for three observations, at 12, 24, and 36 hours, respectively. Under the head "development" the length of the germ tubes of spores showing an average development is given in micromillimeters.

These data not only show that cultures having *water* in the bottom of the cells are unreliable and vary according to the *amount* of water present, but that "dry" cells are equally unsatisfactory. Especial attention is called to the record of the cultures labeled "A 10". Here we have a solution of KCN which is but one-fourth the strength of that in "A 9", the former, however, had several drops of the *n*/128 KCN solution placed in the bottom of the cell, the latter had water only. The striking difference in the result needs no comment. The results with *Penicillium* and other forms abundantly confirmed the test, and lead to the conclusion that *when water is used at the bottom of cells containing hanging-drop cultures and solutions of substances having very high vapor pressures are being tested, erratic germinations are to be expected; and in the case of a test of any substance — particularly those of high or low vapor-pressure — the toxic properties shown will be less than a correct method would indicate.*

In the regular work reported in this paper, a few drops of the same solution as that used in the hanging-drop of any particular cell was in every case placed in the bottom of that cell, thus establishing complete equilibrium of vapor-pressures in the cells and preventing changes in the concentration of the solutions being tested, as must take place where this precaution is not observed. By this means it was found quite feasible to make hanging-drop cultures of any composition whatever, ranging from 16*n*/1 (70 percent) solution of alcohol to a 4*n*/1 (21 percent) solution of potassium hydroxide.

6. *Stock Solutions of Chemicals.* — These were prepared in each case by a responsible chemist in rather concentrated solutions. The stock solution of HCl, for example, contained 25 grams pure HCl per 100 cc. *n*/1-HCl contains 3.58 percent HCl by weight. Such a solution was gotten by taking 5 cc. of stock solution and diluting, by adding beet infusion, to 34.9 cc. *n*/2 was gotten by diluting 10 cc of *n*/1 to 20 cc, and so on. Chemical agents liable to deteriorate in quality (e. g. KCN) were titrated by the chemist on the morning of the day on which the cultures with it were made up.

7. *Trial and Regular Cultures.* — Inasmuch as the work was, in most cases, of a pioneer character, it was found desirable to make up a larger number of trial cultures preliminary to the regular work in order to get some definite idea as to the toxicity of the various chemicals to this group of plants; for it was of course early learned that the data worked out for the phanerogams by Kahlenberg and True[1] and by Heald[2] were a contrast rather than a comparison when placed beside the facts learned by experiment from the fungi. Heald[3] indeed called attention to this fact in 1896, when he found a fungus growing vigorously in a solution of HCl that had killed the root of *Pisum*. The data obtained from the trial cultures proved invaluable in making up the regular cultures, as it was then possible, in most cases, to make up a series of twelve dilutions, in No. 1 of which the spores would certainly be killed while in No. 12 the fungus would be practically unharmed.

In the regular work all cultures were made up in duplicate, including duplicate checks in pure beet infusion. Important points were quite frequently checked over in duplicate and sometimes in quadruplicate. This was also done in the case of *unexpected* developments; for instance, the writer was surprised to find the spores of *Penicillium* showing so great a specific resistance to acetic acid. Repeated checking, however, proved the correctness of the first observation.

[1] Kahlenberg and True, loc. cit.
[2] F. D. Heald, loc. cit.
[3] Ibid., p. 130.

One of the most marked features of the entire work was the *regularity in results.* It is true that the cultures nearest the inhibiting point in a few cases varied to the extent that germination of a number of spores took place in one culture while the duplicate failed. Such were not considered *erratic.* If, however, both cultures of a certain strength grew and one of some weaker concentration failed, the latter would be considered "erratic". Such erratic cultures, however, did not number a dozen in a work requiring upwards of forty-five hundred regular cultures, aside from preliminary work. Such as did occur were no doubt due to oversight in cleaning cells or to other accident.

8. *Examination of Cultures, Noting Results, etc.,* — Cultures were made up in the early part of the day, and were examined at intervals of from 3 to 6 hours for the fourteen hours following and at longer intervals until the fungus had matured or the spores in the cultures which had failed to germinate, were transferred to pure beet infusion to test their vitality. The percentage of spores germinated in the various cultures was noted on two occasions, first when from 30 to 70 percent of those in the checks had germinated and again a few hours later. A similar method was adopted to indicate the early mycelial development. At some time after germination the germ tubes showing an average development were measured and noted; this was repeated a few hours later, and sometimes a third measurement was made. The first appearance of conidia was also noted, but as this very frequently occurred at night (between 15 and 22 hours after inoculation) the point was not so well noted.

In the earlier work, the cultures in which the spores *failed to germinate* were opened at 72 hours[1] and a number of the spores were transferred by means of a sterile platinum needle to a hanging drop of pure beet infusion in a clean cell, in order to test whether they were killed by the agent or whether their germination was merely inhibited. If one percent or more survived they were classed as *inhibited;* if none at all, or less than

[1] Cultures in alcohol, formaldehyde, H_2O_2, and KCN were transferred at 72 hours; all others at 48 hours.

one per cent survived, they were classed as *killed*. In most of the work, however, the transfers were made at 48 hours, it being found that all spores that could germinate did so in less than 36 hours, and usually much earlier.

The cultures which germinated in the presence of the deleterious agent were likewise divided into two classes: (1) those which, although they may have been retarded or stimulated in mycelial development by the agents, finally matured a fair crop of conidia in about the normal time; (2) those which, although they germinated and continued to grow, presented a markedly irregular or retarded mycelial development, and generally failed to fruit. Between these two classes came — as might be supposed — a number of cultures which it was very difficult to classify. In some cases there would be an apparently normal mycelial development but almost total suppression of fructification. In other cases an irregular, meager, and even yeast-like mycelium would cause surprise by finally developing a number of apparently normal fruits. In general, a fungus was said to be "injured" by that concentration of the deleterious agent which prevented its classification in class 1 as above.

In discriminating between class 3 (inhibited spores) and class 4 (killed spores) attention is again called to the importance of avoiding *bunches* of spores in making the inoculation. In many solutions such bunches — doubtless containing air — float on the surface of the drop and fail to receive the full influence of the agent. Where spores from such a culture are transferred to pure beet infusion to test their vitality the bunch may be broken up in the process and the spores germinate readily while all others are dead. Much can be done by care in inoculating, but at best it is a serious source of error, and it has been on this account and on account of the impossibility of transferring the spores without taking with them small quantities of the agent that the *inhibiting point* rather than the death-point has been adopted as the *chief critical point* in discussing the experimental data.

To illustrate what has been said regarding the taking of notes on cultures, a typical left-hand page of the culture note-book (duplicate cultures omitted) is here presented. This may also

Aspergillus IN BEET INFUSION + $CoSO_4$

Cultured at 9 A. M., Feb. 21st, 1899 — Temperature 28° C

Class	Number of culture	Culture label	Strength of solution	Germination hrs	Germination pct	Germination hrs	Germination pct	Mycelial development hrs	Mycelial development μ	Mycelial development hrs	Mycelial development μ	Mycelial development hrs	Mycelial development μ	Fruit hrs	
I	2479	A1	$-CoSO_4$	6	85			6	30	12	200	22	∞	22	(N. B. Record of duplicates omitted to conserve space.)
I	2481	A2	$\frac{n}{2048}$	6	80			6	30	12	210	22	∞	22	
I	2483	A3	$\frac{n}{1024}$	6	85			6	30	12	200	22	∞	22	
I	2485	A4	$\frac{n}{512}$	6	80			6	30	12	180	22	∞	27	
I	2487	A5	$\frac{n}{256}$	6	75	8	100	6	25	12	170	22	∞	27	
Intermediate.	2489	A6	$\frac{n}{128}$	8	50	12	100			12	60	22	∞	36	
Intermediate.	2491	A7	$\frac{n}{64}$	12	1	22	100					22	170	48	Well fruited at 72 hours
II	2493	A8	$\frac{n}{32}$	22	1	36	2					22	15	72	Few fruits only
III	2495	A9	$\frac{n}{16}$	[Transferred at 48 hrs; 12 hrs 5 pct germ.; 24 hrs Many more]											
IV	2497	A10	$\frac{n}{8}$	["		" "	"	Failed]							
IV	2499	A11	$\frac{n}{4}$	["		" "	"	"]							
IV	2501	A12	$\frac{n}{2}$	["		" "	"	"]							

help the reader to understand the classification of the experimental data presented later. The opposite page was always reserved for more extended notes on points observed from time to time in the progress of the experiment.

9. *Sources of Error.* — Before proceeding to a discussion of the experimental data it might be well to mention briefly the sources of error observed during the preliminary study and guarded against in the progress of the work.

1. Xylonite cells were found to have an injurious influence on some fungi when used for hanging-drop cultures at 28° C.

2. Bacterial contamination.

3. Lack of equilibrium in vapor pressures in cells.

4. Deterioration of stock solutions. (See details of experiment with KCN.)

5. The use of impure vaseline in sealing cells.

6. Use of spores of uncertain age and quality.

7. Use of a culture medium unsuited for the normal development of the fungi tested.

8. Imperfect sealing of cells, due to the raising of the cover by expansion of contained air when cultures were placed in the thermostat.

9. Transference of bunches of spores in inoculating cultures.

III. EXPERIMENTAL DATA AND DISCUSSION

Details regarding the critical points (i. e. concentrations causing injury, inhibition, and death) of the various fungi in the more important of the thirty-seven compounds tested may be found in the diagrams, Figs. 1–4. These give in condensed form the various specific resistances of the different molds and it is hoped that they will also be useful in conveying to the reader by means of the eye a general impression as to the relative toxic powers of the various agents. It should be distinctly borne in mind in consulting the diagrams that each vertical line represents a *doubling* of the number of molecules present in the solutions as you pass towards the right, the whole space between two

vertical lines representing one concentration. In the diagrams horizontal dashes denote that the mold was killed by those concentrations; a continuous horizontal line denotes inhibition of the spores; a dotted line denotes injury, while alternating dots and dashes indicate that the solutions permitted practically normal development. As has previously been stated, the dividing line between these last two classes is not sharp and, in some cases therefore, two sets of lines are used for a given concentration. To make the diagrams a little clearer the most dilute solutions that yet kill are connected by a line; the same is done with the most dilute solutions, that yet inhibit and with the most dilute solutions that yet cause injury. The letters in a vertical line at the left stand for the different fungi, A, S, Œ, B, and P representing *Aspergillus*, *Sterigmatocystis*, *Œdocephalum*, *Botrytis*, and *Penicillium*, respectively.

In the general discussion details will be omitted except where they are thought to be especially worthy of note, or are significant from a biological or a chemical point of view.

ACIDS.

Hydrochloric Acid, HCl, 70, *230*, 614. — This acid, on account of its very high dissociation at the critical points and because of its very wide use in physiological and chemical investigations by other workers, has been taken as a *standard* by which we shall compare the others. In making these comparisons, HCl being the most highly dissociated of all acids, is assumed to represent the value of ionic $\overset{+}{H}$. In other words, we have, for the sake of getting a basis for comparison, assumed that the 9

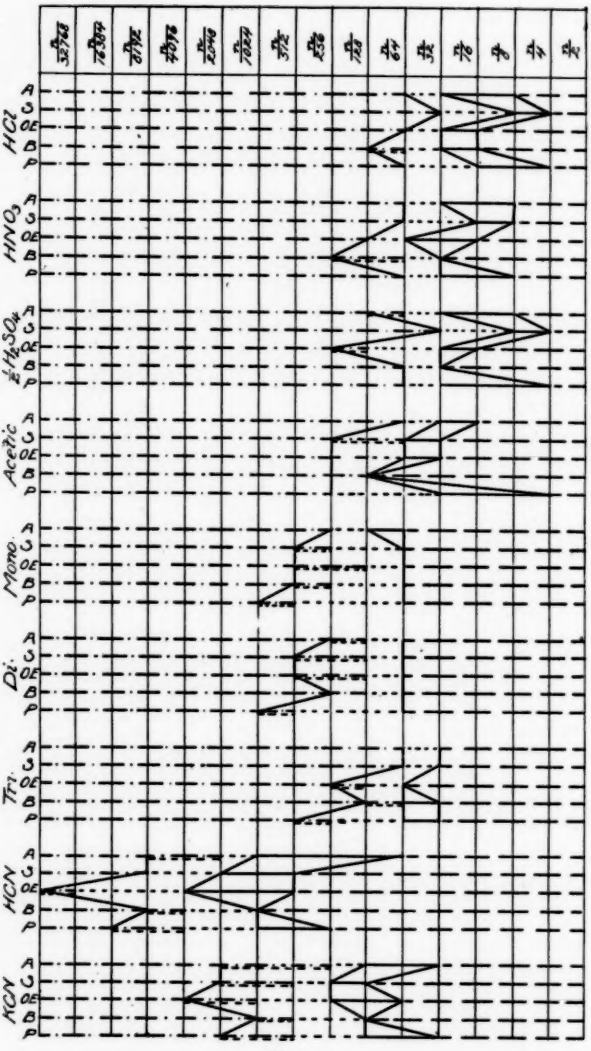


Fig. 1

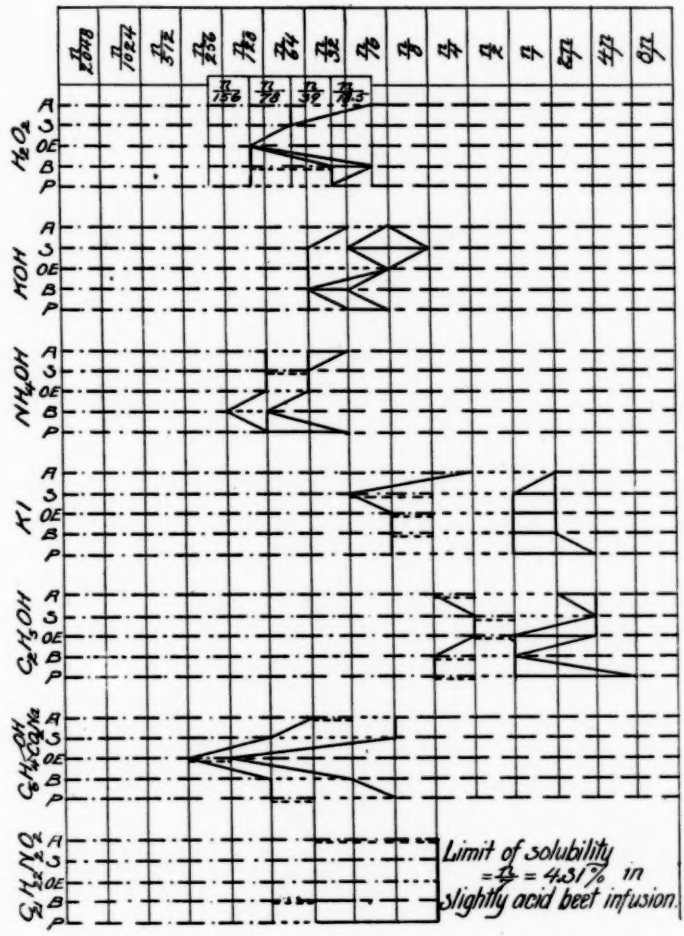

1/2048
1/1024
1/512
1/256
1/128
1/64
1/32
1/16
1/8
1/4
1/2
1
2
4
8
16
H2O2
MOH
NH4OH
KI
C2H5OH
C6H5COONa
C6H12N2O2
A
J
OE
B
P
Limit of solubility
= 1/4 = 4.31% in
slightly acid beef infusion.

Fig. 2

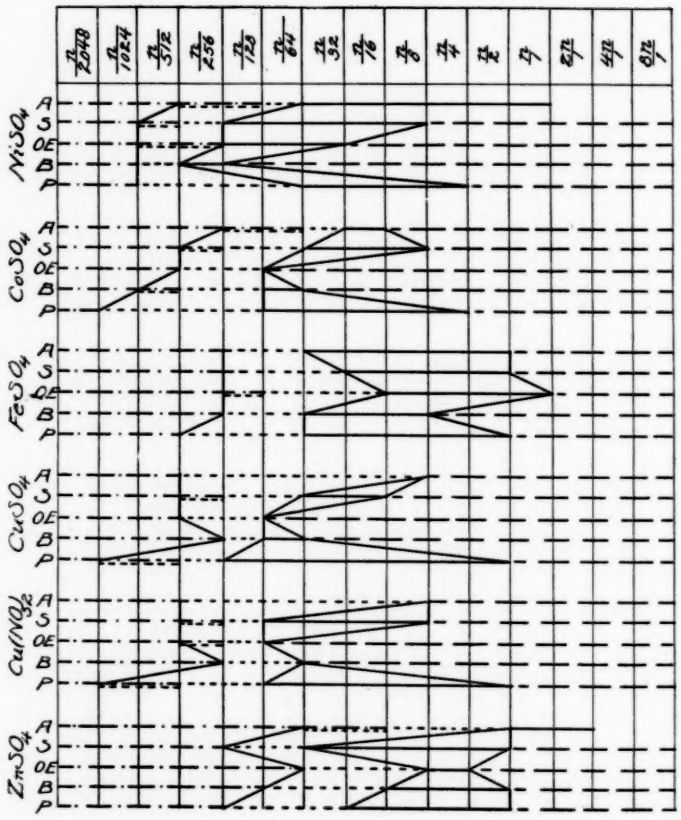

1/2048
1/1024
1/512
1/256
1/128
1/64
1/32
1/16
1/8
1/4
1/2
1
2/1
4/1
8/1
NiSO4
CoSO4
FeSO4
CuSO4
Cu(NO3)2
ZnSO4
A
S
OE
B
P

Fig. 3

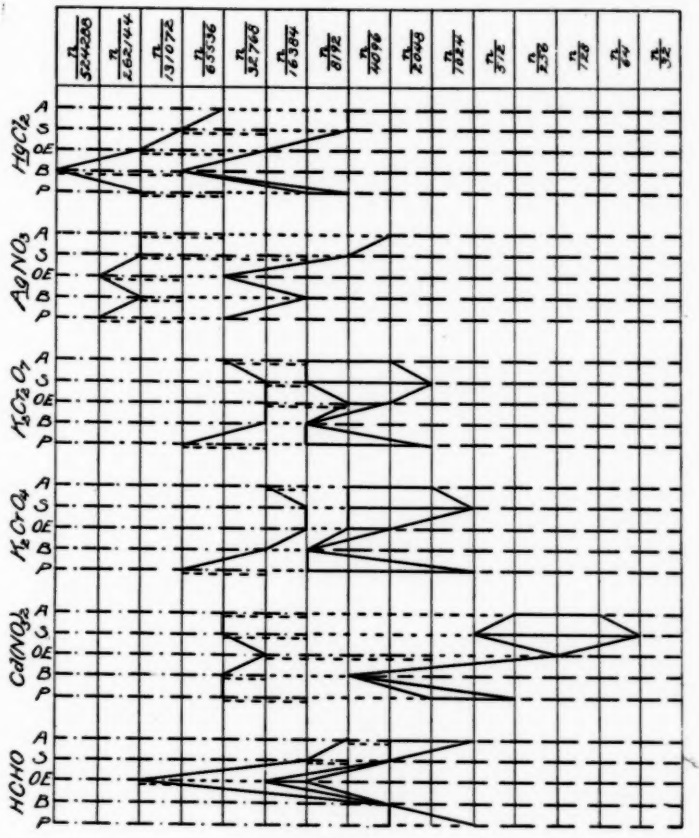


Fig. 4

percent of HCl which is still undissociated at the inhibiting point for the molds, has the same toxic value as ionic H^+. This is a purely arbitrary assumption, and the reader is requested to bear in mind that when we speak of the toxic value of ionic H^+ we mean the *nearest approach* we could make to determining its toxic value for fungi, viz. *that of 91 percent ionic* H^+ + *9 percent* HCl.

By referring to page 275 it will be noticed that the following "coefficients" have been worked out for HCl with these five molds:

Coefficient of injury,		70
"	" inhibition,	230
"	" death-point,	614

These coefficients mean that on *an average for the five forms used* 70/2048 of a normal solution caused distinct injury to the cultures, 230/2048 of a normal solution inhibited the germination of the spores, and 614/2048 of a normal solution killed the spores. The denominator, 2048 — the eleventh power of 2 — has been used throughout this paper in determining coefficients. As a matter of convenience the numerator only has been expressed in discussing the three critical points of the various agents, giving as it does at a glance the correct *relative* toxicity of the agents. The *absolute* value of any coefficient may (in either mold or agent) be determined by simply supplying the omitted denominator, 2048, the resulting fraction being in every case that proportion of a normal solution. In discussing the various agents these coefficients will be placed immediately after the chemical formulae in the order given. That expressing the inhibiting value is *italicized* to emphasize the fact that it is regarded as the most significant.

On the whole, HCl was at the same time the most completely dissociated and the least toxic of the acids tested.

From time to time attention will be called to the wonderful resistance of the fungi as compared with that of the higher

plants to many deleterious agents. The comparison (or contrast?) in resistance to ionic $\overset{+}{H}$ is as 800 to 1, the average death-point for the five species of molds being $n/3.3$ HCl, while that of three species of phanerogams is $n/2740$ HCl.[1]

Sterigmatocystis proved most resistant to ionic $\overset{+}{H}$, for although germination and early mycelial development was distinctly retarded by $n/1024$, $n/4$ was required to inhibit all the spores, and $n/2$ for forty-eight hours to kill them. Cultures in $n/16$ although much retarded in early development, had produced at 48 hours a mycelium equal to the checks, and at 72 hours far surpassed them in mycelial development. Retardation of fruiting was first noticed in $n/128$; $n/16$ required nearly double the time to mature its fruit as compared with the checks, while $n/8$, the limiting culture, failed to fruit in six days.

In the case of HCl, as in the case of all other acids tested, an attempt was made to determine the relative toxic value of the anion. The potassium salt was used. This salt becomes highly dissociated into $\overset{+}{K}$ and $\overset{-}{Cl}$ ions in moderately concentrated solutions. In a $n/4$ KCl solution we find 84 percent of the salt dissociated.[2] In a similar concentration of HCl 89 percent is dissociated.[2] In the former we have $\overset{+}{K}$ and $\overset{-}{Cl}$ ions and some KCl; in the latter, $\overset{+}{H}$ and $\overset{-}{Cl}$ ions and some HCl. It is evident therefore that the essential difference between these solutions is the replacing of the $\overset{+}{H}$ in the latter by $\overset{+}{K}$ and the HCl by KCl in the undissociated portion. The significant point is that the *concentration of $\overset{-}{Cl}$ ions is practically the same in both.* The $n/4$ HCl solution is fatal to the spores of *Aspergillus*, while the $n/4$ KCl solution has practically *no injurious influence.* Indeed, the fungus germinates, grows, and fruits normally in a solution of double this concentration of KCl. Hence we know that the $\overset{-}{Cl}$ ion is *relatively harmless* to this mold.

[1] F. D. Heald, 1896, loc. cit. p. 152.

[2] F. Kohlrausch, Wied. Ann. **26**, 195 (1885).

The absolute value of ionic $\bar{Cl}$, and other weakly toxic ions, is, however, very difficult to determine. In the first place the potassium salts of the various acids are — although highly — far from being completely dissociated at the concentrations permitting germination of mold spores. Then, too, we are perhaps not justified in assuming that ionic $\dot{K}$ is entirely non-toxic; for although K is a necessary food element for all plants, may it not be that great concentrations of even so good a thing as ionic $\dot{K}$ may be bad for fungi? Later, this will be shown to be so in the case with iron, an element which while absolutely necessary in small quantities[1] is quite toxic in excess for both fungi and higher plants. Experiments with *Aspergillus* and *Œdocephalum* in KCl solutions, however, enable us to say quite positively that for these forms the anion $\bar{Cl}$ has at most *less* than 1/32 the toxic value of ionic $\dot{H}$, and may therefore be disregarded in a discussion of the toxic properties of HCl.

Nitric Acid, HNO_3, 48, *141*, 384. Dissociated in almost the same proportion as HCl,[2] HNO_3 proved much more toxic. Inasmuch as the concentration of $\dot{H}$ ions is practically the same as in HCl, and the $\bar{NO}_3$ ion being proved to have a toxic value of less than 1/32 that of ionic $\dot{H}$, we must look for an explanation in the toxic value of the undissociated molecule, HNO_3. This was found to be approximately 7.7 times that of ionic $\dot{H}$.[3] In other words, a molecule of HNO_3 loses nearly 7/8 of its toxic properties for molds on becoming ionized. Krönig and Paul[4] found that anthrax spores immersed in a solution of $n/1$ HNO_3 for two hours were entirely destroyed. The same concentration of HCl permitted 385 colonies to survive. In solutions, however, where over 90 percent of the molecules are dissociated these

[1] H. Molisch, Sitzungsber. Akad. Wiss. Wien. **103**, I, (1894).
[2] F. Kohlrausch. Wied. Ann. **26**, 196 (1885).
[3] See table I, page 293.
[4] Krönig and Paul. loc. cit. (1897).

acids showed far *less* variation in toxic properties, although HNO_3 was still distinctly the more toxic. This toxic power of the undissociated molecule, HNO_3, they termed its "specific poisonous effect." That completely dissociated HNO_3 has no "specific poisonous effect" is shown by the fact that it has, when in that condition, exactly the same toxic value as HCl or 1/2 H_2SO_4.[1] The oxidizing power of HNO_3 suggests a possible explanation of its high toxic value. The oxidizing poisons have, as we shall see later, a very powerful influence on mold fungi.

The influence of HNO_3 on germination was much the same as that of HCl, *n*/1024 causing distinct retardation of both germination and early growth. Later, however, marked differences developed. Cultures containing the HNO_3 produced a much heavier mycelium, and fruiting, although slightly, was not greatly retarded.

The stimulation of mycelial development was possibly due to the non-toxic, nitrogenous ion, $\bar{N}O_3$. *The cultures with KNO_3, however, did not establish this view.* Cultures in *n*/1 KNO_3 solutions were not greatly different from those in similar concentrations of KCl and K_2SO_4 although the concentration of $\bar{N}O_3$ ions would in this case be some 40 times as great as in the stimulated cultures of HNO_3 under discussion. The fact that the fruiting was not greatly retarded again suggests the action of an oxidizing agent. It is indeed not improbable that both the marked stimulation and greater toxicity are to be attributed to the properties of the undissociated molecules present.

Sulphuric Acid, 1/2 H_2SO_4, 61, *205*, 589. As will be observed, *n*/1 of this agent is based on the half molecule in order to make it strictly comparable with the other acids used, the others being all monobasic.

H_2SO_4 becomes dissociated first into $\dot{H}$ and $\bar{H}SO_4$ ions, but as dilution increases the $\bar{H}SO_4$ ion further breaks up into $\dot{H}$ and $\bar{\bar{S}}O_4$. The anion $\bar{\bar{S}}O_4$ is practically non-toxic having like $\bar{C}l$

[1] Kahlenberg and True, 1896, loc. cit. p. 92.

and $\bar{N}O_3$ less than 1/32 the toxic value of ionic $\dot{H}$. The dissociation of H_2SO_4 at the inhibiting point is about 62 percent only.[1] Each 100 molecules, then, at this concentration, break up into approximately 124 $\dot{H}$, 76 $\bar{H}SO_4$, and 24 $\bar{S}O_4$ ions. This solution having a greater toxic value than a similar concentration of ionic $\dot{H}$, the excess of toxic properties must be due to the partially dissociated group, $\bar{H}SO_4$. By referring to Table I. it will be seen that the toxic value of this anion is approximately 1.3 in terms of ionic $\dot{H}$.

In this as in the other mineral acids, *Sterigmatocystis* showed the greatest resistance, $n/2$ being necessary to kill. *Botrytis* was the most sensitive, $n/16$ H_2SO_4 being fatal.

Acetic Acid, $CH_3.COOH$, 25.6, *83*, 314. This acid at the inhibiting point, $n/24$, is but 2 percent dissociated.[2] The toxic value of the anion was found to be about 1/13 $\dot{H}$, but as so small a portion of the acid is dissociated the influence of the anion may be disregarded. The properties of this acid are therefore to be attributed almost solely to the undissociated molecule, $CH_3.COOH$, which proves to have a toxic value of 2.8 $\dot{H}$.

Penicillium showed a marked specific resistance to this acid, requiring $n/2$ for 48 hours to kill. This observation was accepted only after repeated trials. *Botrytis*, on the other hand, was particularly susceptible, $n/64$ being fatal. That acetic acid should prove so much more toxic to fungi than the mineral acids was not anticipated.[3] Heald[4] found that it had but 1/8 the toxic value of $\dot{H}$ on *Zea*, and 1/4 on *Pisum*, while Kahlenberg and True[5] found about the same relation with *Lupinus*.

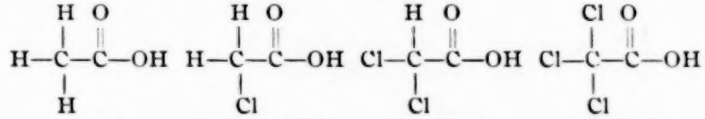
The great variation in protoplasmic resistance to this acid is shown by the following data: The vinegar eel — *Rhabditis*

[1] Kohlrausch. Wied. Ann. **26**, 196 (1885).
[2] Ibid, **26**, 197 (1885).
[3] Migula. Bot. Central. **41**, 207 (1890).
[4] F. D. Heald, 1896, loc. cit, p. 130.
[5] Kahlenberg and True, 1896, loc. cit, p. 110.

aceti — thrives in a $n/2$ solution, which is fatal to *Penicillium* spores. *Aspergillus* spores are killed by $n/8$ and those of *Botrytis* by $n/64$; $n/200$ is fatal to *Zea*, $n/1600$ to *Pisum*.

It is of interest to note in this connection that not only are great differences to be expected between different organisms in their resistance to deleterious agents, but different individuals of the same genus and species may have very different powers of resistance, depending largely no doubt on previous environment. Pfeffer,[1] for instance, grew *Aspergillus* on a nutritive medium containing 8 percent dextrose and one percent acetic acid, and found that the fungus assimilated a far larger amount of the acid than of the dextrose. It will be noted that $n/8$ or 0.7 percent acetic acid proved fatal to the spores of *Aspergillus* used in this study, and in a 0.17 percent solution less than one percent germinated.

The Chloracetic Acids. These acids are formed by replacing one, two, and three atoms of H, respectively, in the acetic acid radical by the element Cl; thus, —



It is a rule that the halogen substitution-products of carbon compounds have a toxic value which bears a close relation to the number of H atoms in the organic radical or hydrocarbon which have been replaced by the halogen. To quote from Davenport:[2] "Beginning with methane, CH_4, we find this substance — marsh gas — innocuous when mingled with air. As the H atoms become replaced by one or more Cl atoms, the poisonous properties increase, —

CH_3Cl is slightly anaesthetic.
$CHCl_3$ = chloroform.
CCl_4 is very dangerous, stupefying involuntary muscles".

[1] Jahrb. f. wiss. Bot. **28**, 205 (1895).
[2] Experimental Morphology I, 8 (1897).

Many other examples illustrating this rule might be quoted. It was a matter then of great surprise to find what, at first sight, seemed to be a direct violation of this rule in the action of the chloracetic acids on the mold fungi. Their critical points were determined as follow:

(Acetic acid	25.6	*83*	314)
Monochloracetic	8.8	*58*	64
Dichloracetic	10.4	*64*	64
Trichloracetic	37	*90*	115

As soon as the experiment was complete the stock solutions used were placed in the hands of a chemist who formed the potassium salt of each by just neutralizing with KOH. These salts are all quite highly dissociated, the cation being ionic K^+, and the anion the acid radicals of the respective acids. The toxic values of these anions, as nearly as could be determined with *Aspergillus* and *Œdocephalum* were as follow:

Monochloracetic	$-CH_2ClCOO$	1/32 of ionic H^+.
Dichloracetic	$-CHCl_2COO$	1/21 " " H^+.
Trichloracetic	$-CCl_3\ COO$	1/11 " " H^+.

Here the toxic values, although not high, are in the expected order.

Let us glance at the toxic value of these acids in a practically completely dissociated condition. Kahlenberg and True[1] found that with Lupinus *n*/6400 monochloracetic was not fatal; *n*/6400 dichloracetic was evidently on the line, one plant being, killed, while the check survived; *n*/6400 trichloracetic proved fatal. The dissociation being practically complete we have to deal with ionic H^+ and the anions only. Monochloracetic with its non-toxic anion gives for *Lupinus* the same critical concentration as HCl; dichlor- and trichloracetic are increasingly but not greatly more toxic. This increase in toxicity is probably due entirely to the anions.

At the concentrations at which they are effective towards

[1] Kahlenberg and True. Loc. cit. p. 113.

the molds, however, we have an entirely different condition as regards dissociation, as is seen from the following: —

Monochlor.	inhibits at	$\frac{n}{35}$	and is	20	percent	dissociated.[1]	
Dichlor.	"	" $\frac{n}{32}$	"	"	70	"	"
Trichlor.	"	" $\frac{n}{22.8}$	"	"	88.8	"	"

This variation in the dissociation is the key to the explanation of the apparent deviation from the rule referred to above.

That the undissociated molecules are no exception to the rule is shown in Table I, page 393, where the toxic values of the different molecules are shown to be approximately as follow:—

Monochloracetic	acid	4.7	times	value	of	ionic	H.
Dichloracetic	"	9.5	"	"	"	"	"
Trichloracetic	"	14.1	"	"	"	"	"

The introduction of Cl into the acetic radical results in two distinct changes in the chemical and physical properties of the acid: (1) A great increase in the toxic properties of the undissociated molecule. (2) A great increase in the dissociation of the acid in aqueous solution of given concentration. That the greater dissociation often masks the effect of the increase in the toxic properties of the undissociated part is easily understood when we recall that the toxic value of the dissociated portion of an acid cannot be greater than the value of ionic H plus the value of the anion.

Putting all together, we get in brief the following: (1) The replacement of one H in the acetic radical doubles the toxic properties of the undissociated portion, and increases the dissociation in a $n/35$ concentration from two percent to twenty percent. The net result of these conflicting factors is an increase in toxic properties for this concentration of about 40 percent. (2) The replacement of two H's by Cl more than trebles the toxicity of the undissociated molecule, and causes dissociation to advance from two percent to 70 percent in a $n/32$ concentration. This gives

[1] Ostwald. Zeit. phys. Chem. **3**, 176 (1889).

a net increase of about 30 percent in toxic value for this concentration. (3) When all three H atoms are thus replaced by Cl the undissociated molecule has a toxic value of over five times its original value, and dissociation advances from 2 percent to 88.8 percent in a $n/22.8$ solution. At this concentration the effect of the greater dissociation is more than can be made up by the increased toxic value of the comparatively few remaining undissociated molecules, hence a *decrease* in the toxic properties of this acid in $n/22.8$ concentration as compared with the original acetic acid.

These empirical results enable us to approximate mathematically the toxic values of these acids at any concentration provided that we know the extent to which dissociation has proceeded at that concentration, thus,

(1) Molecule of acetic acid = 2.8 $\overset{+}{H}$; dissociation at $\frac{n}{35} = 2.4\ \%$

" monochlor. " = 4.7 $\overset{+}{H}$; " $\frac{n}{35} = 20$ pct

(a) Increase in toxic value = 1.9 $\overset{+}{H}$ in 80 pct of acid = 152 units.

(b) Decrease due to dissociation = 1.8 $\overset{+}{H}$ in 17.6 pct of acid = 32 units.

Resultant of these two factors = 120 units *increase.*
Toxic value of acetic acid = 277 "

Total calc. for $\frac{n}{35}$ monochlor. = 397 "
Value found experimentally = 396 "

(2) Molecule of acetic acid = 2.8 $\overset{+}{H}$; dissociation at $\frac{n}{32} = 2.36$ pct

" dichloracetic " = 9.5 $\overset{+}{H}$; " $\frac{n}{32} = 70$ pct

(a) Increase of toxic value = 6.7 $\overset{+}{H}$ in 30 pct of acid = 201 units.

(b) Decrease due to dissociation = 1.7 $\overset{+}{H}$ in 67.6 pct of acid = 115 units.

Resultant of these two factors = 86 units *increase*
Toxic value of acetic acid = 277 "

Total calc. for $\frac{n}{32}$ dichloracetic = 363 "
Value found experimentally = 359 "

(3) Molecule of acetic acid = 2.8 $\overset{+}{H}$; dissociation at $\frac{n}{22.8}$ = 2 pct

" trichloracetic = 14.1 $\overset{+}{H}$; " $\frac{n}{22.8}$ = 88.8

(a) Increase of toxic value = 11.3 $\overset{+}{H}$ in 11.2 pct of acid = 126.6 units.

(b) Decrease due to dissociation = 1.55 $\overset{+}{H}$ in 86.8 pct of acid = 134.5 units.

Resultant of these two factors = 7.9 units *decrease*
Toxic value of acetic acid = 277.0 "

Total calc. for trichloracetic acid at $\frac{n}{22.8}$ = 269.1 units

Value determined experimentally 255 units.[1]

The addition of any highly dissociated acid to a solution of a " weaker " acid throws back the dissociation of both, but more especially that of the one having the low dissociation. This method of decreasing the dissociation, and thereby increasing the toxic properties, was used with di- and trichloracetic acids. A complete series of cultures with all five molds were made up in solutions of these acids containing in addition an equal concentration of HCl molecules.

Dichloracetic acid has a toxic value of 359 units as compared with 100 for HCl. Now, if to a solution of dichloracetic acid we add hydrochloric acid — molecule for molecule — we should expect the resulting mixture to have a toxic value of 359 + 100 + *the increased toxic value of the molecules of the acids which would be forced back to the molecular from the ionic state by the increased concentration* of $\overset{+}{H}$ ions. Dichloracetic acid would under these circumstances and at the concentrations used have its dissociation reduced approximately 20 percent. The undissociated molecule having 8.4 units *more* toxic value than when dissociated, we should expect to find its quota towards

[1] This possibility of calculating mathematically the toxic properties of a given concentration of an acid occurred to the writer only after this paper had been prepared for the press. The agreement between the calculated and experimental values was so striking, however, that it was thought advisable to insert the comparison at this place. Too much importance must not, however, be attached to the exact numerical values here given for the undissociated molecules. These doubtless vary with different plants.

increasing toxicity to be $8.4 \times 20 = 168$ units. Disregarding then the effect of the forcing back of the ionization of the HCl — the relative toxic value of whose molecule we have been unable to estimate — we have the following:

Toxic value of dichloracetic acid	= 359 units
" " " hydrochloric "	= 100 "
Calc. increase in toxicity of the former	= 168 "
Total toxic value anticipated	= 627 "

The experimental test with the five molds gave a toxic value of 606 for the mixture, or an increase of 147 units for the forcing back of the dissociation.

In the case of trichloracetic acid + HCl the variation calculated was less on account of the high dissociation of this acid at the concentrations used. The experimental data, however, placed the toxic properties of the mixtures some 13 units in *excess* of the increase calculated.

Further experimentation along this line will doubtless throw light on the toxic value of the HCl molecule. The indications are that it is not greatly different from that of ionic H^+.

Krönig and Paul's[1] work on anthrax spores is of especial interest here. A preparation of anthrax spores immersed in a normal solution of trichloracetic acid for 2 hours and afterwards cultured in a favorable medium proved to be entirely sterilized, not a spore surviving. In another test where a similar preparation of spores was immersed in the same concentration for 20 minutes comparatively few survived. Tests were also made with the same acid at $n/16$ concentration. Spores immersed for 56 hours in this strength showed much less injury than those immersed for 20 minutes in the $n/1$ solution, thus showing plainly that the *efficacy of the acid was more greatly reduced than could be accounted for by the increased dilution only.* Their work with the other acetic acids, although not extensive, is quite in harmony with the results here recorded for the molds.

Hydrocyanic Acid, HCN, 0.36, *3*, 20. — This poison so

[1] Krönig and Paul, 1897, loc. cit.

deadly to the higher vertebrates has long been known to be much less toxic to less highly organized structures. Extremely fatal to man even in minute quantities, the more lowly organized *Ascaris* resists a 3 percent solution for 75 minutes. A myriapod (*Fontaria*) excretes HCN when irritated. The accumulation of much such data has led to the general acceptance of the theory that HCN acts chiefly or wholly upon the aldehydes of the nerve centres.[1] This is no doubt a perfectly satisfactory theory from the animal physiologist's point of view, but it leaves us without any explanation for its violent toxic properties towards plants where we have no nerve centres.

Little work seems to have been done with it on plants. Kahlenberg and True[2] found that towards *Lupinus* it had double the toxic value of $\dot{H}$, $n/6400$ proving fatal. To the molds, however, it is relatively a much more powerful agent, having 76.6 times the value of $\dot{H}$, thus ranking as one of their most fatal poisons.

The data on the dissociation of this acid is meager. At $n/32$ it gives about 1/16 the electrical conductivity of acetic acid at the same concentration.[3] From this we should judge that the dissociation is practically zero at the concentrations with which we have to deal. The value of the anion $\bar{C}N$ was determined by means of the potassium salt, which is quite highly dissociated.[4] The KCN solutions proved to have nine times the toxic value of ionic $\dot{H}$ for the molds. Allowance being made for the hydrolysis which would take place in the KCN solutions,[5] we find the $\bar{C}N$ ion to have approximately the value of 8 $\dot{H}$. Hence we reason, were HCN wholly ionized into $\dot{H}$ and $\bar{C}N$ ions we should expect its solutions to have a toxic value of approxi-

[1] O. Loew. Ein natürliches System der Gift-Wirkungen, (1893).
[2] Kahlenberg and True, 1896, loc. cit.
[3] Ostwald. Jour. prakt. Chem. (2) **32**, 304 (1885).
[4] Kohlrausch. Wied. Ann. **6**, 149 (1879).
[5] See details with KCN solutions, p. 302.

mately 9 H. The fact that the solutions of this compound in its undissociated form have a toxic value of over 8 times that of the additive toxic properties of its component parts tells for the extremely toxic influence of the molecule HCN.

In Table I the toxic values of the undissociated molecules, as shown by their inhibiting and killing powers towards the spores of these five molds, are approximated.

Too much importance must not be attached to the *exact numerical* value here expressed for the different molecules for several reasons. We do not know the reaction of the acids towards the nutrient medium in which we grow our plants. We do not know the exact effect of the salts and sugars present on the dissociation of the acids. And were it possible to eliminate every factor causing doubt or error, we should undoubtedly find the relative toxic properties of the molecules varying somewhat with almost every species tested. Let me repeat: the exact numerical values here given are *not* significant. The order and general proportions of these values *are* significant.

The emphasis is laid on Part I of this table for reasons already fully stated.

Line 1 gives the strengths of the various acids required on an average to inhibit germination. Line 2 is developed from line 1. It gives the relative toxic properties of the acids expressed numerically, HCl being taken as 100 for a basis for comparison. The dissociated and undissociated portions are considered separately; lines 4, 5, and 6 being devoted to the former, and lines 7, 8, and 9 to the latter. Line 4 gives the toxic value of the cation in terms of ionic H; line 5 that of the anion. Line 6, being the total of 4 and 5, gives that portion of the total toxic value of the acid which is to be attributed to the dissociated portion. Line 7 gives the "residual units" or in other words that part of the total toxic value not accounted for by the dissociated part and hence due to the undissociated portion. Line 8 gives the percentage of the acids still in the molecular state at the critical concentration causing inhibition of germination. Line 9, the quotient of the residual units divided by the percentage of

TABLE I

Relative Toxic Properties of Undissociated Molecules

I. As measured by their inhibiting powers

HCN	$\frac{1}{2}H_2SO_4$	HNO_3	Tri	Di	Mono	Acetic	HCl	Acid	
7 $\frac{n}{683}$	$\frac{n}{10}$	$\frac{n}{14.5}$	$\frac{n}{22.8}$	$\frac{n}{32}$	$\frac{n}{35}$	$\frac{n}{24}$	$\frac{n}{8.8}$	Concentration inhibiting germination	
666	112	163	255	359	396	277	100	Relative toxic value. HCl = 100 units	
—	62	90.6	88.8	70	20	2		Pct dissociated at inhibiting point	
—	62	90.6	88.8	70	20	2		Toxic value of the cation in terms of ionic $\overset{+}{H}$	Dissoc.
—	—	—	8	3.3	.6	—		Toxic value of the anion in terms of ionic $\overset{+}{H}$	
—	62	90.6	96.8	73.3	20.6	2		Total, anion + cation	
7666	50	72.4	158.2	285.7	375.4	275		Residual units	Undis.
100	38	9.4	11.2	30	80	98		Pct undissociated	
76.6	*1.3*	*7.7*	*14.1*	*9.5*	*4.7*	*2.8*		*Toxic value of undis. mol. in terms of ionic $\overset{+}{H}$*	

II. As measured by their killing powers

HCN	$\frac{1}{2}H_2SO_4$	HNO_3	Tri	Di	Mono	Acetic	HCl	Acid	
$\frac{n}{102}$	$\frac{n}{3.5}$	$\frac{n}{5.3}$	$\frac{n}{18}$	$\frac{n}{32}$	$\frac{n}{32}$	$\frac{n}{6.5}$	$\frac{n}{3.3}$	Concentration killing spores	
070	104	160	534	960	960	196	100	Relative toxic value. HCl = 100 units	
—	54	90	88	70	19.9	1		Pct dissociated at death-point	
—	54	90	88	70	19.9	1		Toxic value of cation in $\overset{+}{H}$	Dissoc.
—	—	—	8	3.3	.5	—		Toxic value of anion in $\overset{+}{H}$	
—	54	90	96	73.3	20.4	1		Total, cation + anion	
3070	50	70	438	887	940	195		Residual units	Undis.
100	46	10	12	30	80.1	99		Pct undissociated	
30.7	*1.1*	*7*	*36.5*	*29.6*	*11.7*	*1.97*		*Toxic value of undissociated molecule in $\overset{+}{H}$*	

undissociated molecules, gives in terms of ionic H^+ the toxic value of the different acid molecules.

Part II of this table is worked out similarly and has reference to the toxicity of the acids towards the molds as shown by their power to *kill* the spores.

All acids tested retard germination and early growth of the mold fungi. This retarding influence was evident in greater dilution with the mineral than with the acetic acids. Cultures not greatly retarded almost invariably take on new life not many hours after germination, and presently overtake and surpass the checks in mycelial development. This excessive development of mycelium usually reaches its maximum in cultures two or three removes from the concentration inhibiting germination, and is usually accompanied by retardation of fruiting. In other words, 1/4 to 1/8 the lethal concentration has a strong stimulating influence on the mycelial development, and tends to suppress or at least retard fructification.

Smaller quantities of acid proved on an average to be injurious to *Œdocephalum* than to the other forms, 20/2048 normal being on the average distinctly detrimental. The coefficients of the other forms were as follows: *Botrytis*, 23; *Penicillium*, 28; *Aspergillus*, 42; *Sterigmatocystis*, 64.

Œdocephalum was also the most easily inhibited, its relative inhibiting coefficient being 72, followed by *Botrytis*, 76; *Penicillium*, 100; *Aspergillus*, 104; and *Sterigmatocystis*, 200.

Botrytis, however, was the most easily killed. The order in this respect was *Botrytis*, 100; *Œdocephalum*, 137; *Aspergillus*, 272; *Sterigmatocystis*, 369; and finally *Penicillium*, whose spores showed by far the greatest resistance, represented by the coefficient 498. This high resistance of *Penicillium* in regard to the death-point may be partly due to the tendency of the spores to adhere in bunches in making the inoculation, a difficulty never fully overcome.

The bearing of these results on the modern theories of the chemical and physiological action of substances in aqueous solution is of sufficient importance to demand a brief treatment.

A close connection between the electrical conductivity and the chemical activity was first noticed by Hittorf (1853), but it remained for Arrhenius[1] to point out the numerical comparison. This rather close numerical agreement between the *dissociation of the acids* and their *chemical action* may be noticed in the first five lines of the accompanying table. These lines represented the most important data available until the appearance of Levy's[2] paper in 1895.

Line 1 gives the relative dissociation of normal solutions of these acids (except HCN), HCl being taken as a standard as it is in all the tests recorded in this table. Line 2 gives the relative powers of the different acids to promote the well-known catalysis of aqueous solutions of methyl acetate. Line 3 gives their relative activity in decomposing calcium oxalate. Line 4 gives Ostwald's determinations of their relative affinities for hydroxides. Line 5 gives their relative activity in inverting cane sugar.

The correspondence between the figures in these five lines is certainly quite striking, especially when it is remembered that the solutions used in the different tests were not of the same concentration. Allowance must also be made for the experimental difficulties involved in chemical measurements. Under these circumstances it is not strange that many chemists came to the conclusion that it is *the ionized part of a dissolved substance and that only* which is chemically active. To quote from Whetham :[3] "We may take it, then, that only that portion of a body is chemically active which is electrolytically active — that ionization is necessary for chemical activity just as it is necessary for electrolytic conductivity."

What applies to chemical activity must also apply to physiological activity for in its ultimate analysis the latter is doubtless due to the former. Kahlenberg and True[4] remark, "It has always been taken as axiomatic that the physiological action of any substance is due to its chemical character."

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[1] Arrhenius. Recherches sur la conductivité galvanique des Électrolytes, Stockholm (1883).

[2] A. Levy. Zeit. phys. Chem **17**, 317 (1895).

[3] W. C. D. Whetham, loc. cit, p. 165.

[4] Kahlenberg and True, loc. cit, p. 85.

TABLE II

CHEMICAL AFFINITIES OF ACIDS.

HCN	Trichlor	Dichlor	Monochlor	Acetic	$1/2H_2SO_4$	HNO_3	HCl	Acid
—	62.3	25.3	4.9	1.4	65.1	99.6	100	Relative dissociation of $\frac{n}{1}$ sol.[1]
—	68	23	4.3	.34	74	92	100	Catalysis of methyl acetate.[1]
—	63	18	5.1	1	67	110	100	" " calcium oxalate.[1]
—	82	34	7.2	1.2	68	102	100	Neutralizing hydroxides.[2]
—	75.4	27	4.9	.4	73	100	100	Inversion of cane sugar.[3]
—	96.7	62.4	17.2	4.7	71.9	99	100	Multirotation of glucose.[3]
200+	200	100+	100	25	100	100	100	Toxicity for Lupinus.[4]
7666	255	359	396	277	112	163	100	" " molds.

[1] W. C. D. Whetham, '95, loc. cit, p. 164.
[2] Lehrbuch der allg. Chemie (1891).
[3] A. Levy, '95, loc. cit.
[4] Kahlenberg and True, '96, loc. cit.

The uniformity of the results recorded in lines 1–5 is sadly marred by the results of Levy's[1] work recorded on line 6. It will be seen that here all acids have *not* "specific coefficients of affinity ... based on the fact that the relative affinities of different acids are the same whatever the nature of the action by which they are compared".[2] On the contrary Levy found that acetic, mono- and dichloracetic gave results which in round numbers, are 200 percent in excess of what would be calculated by the theory that the dissociated portion only is chemically active. In the case of the highly dissociated trichloracetic the variation from that required by the theory is less, as its physiological action on fungi is less. The toxic properties towards phanerogams (line 7) are equally impossible to harmonize with the theory. The climax, however, is reached in the data presented on line 8, where we are dealing with concentrations which contain in many cases a very large proportion of undissociated molecules.[3]

The chemical reactions involved in physiological investigations are doubtless vastly more complex than is the case in the earlier studies recorded on lines 2–5. In the data (recorded on lines 6–8) derived from the action of the acids on the more complex carbon compounds, and the highly complex aldehydes, albuminoids, etc., found in the protoplasm of living cells, we surely find a very great exception to the alleged law that "the relative affinities of different acids are the same whatever the nature of the action by which they are compared." The affinities, indeed, appear in some cases to be almost the converse of that required by the theory that "only that portion of a body is chemically active which is electrolytically active."

HYDROXIDES

As it is quite impossible to handle solutions of hydroxides in an ordinary atmosphere without a greater or less loss by neutralization by the CO_2 of the air, the following values for caustic potash and ammonia must be regarded as being somewhat less

[1] A. Levy, loc. cit, p. 317.
[2] W. C. D. Whetham, loc. cit. p. 162.
[3] See Table I, p 293.

than their absolute toxic value. This source of error was reduced as much as possible by rapid handling in making cultures.

Potassium Hydroxide, KOH ; 77(?), *166*, 282. In no other case was it so difficult to determine where to place the coefficient of injury. $n/572$ retarded germination in all cases, and in some forms $n/1024$ and even $n/2048$ (*Œdocephalum*) showed an injurious influence. In less than 24 hours, however, the less retarded cultures had as a rule overtaken or surpassed the checks in mycelial development. This stimulation of mycelial development was marked with all forms in $n/2048$, and reached its climax in $n/64$ or $n/32$ concentrations, and was accompanied as usual by retardation of fruiting. This agent caused the production of a denser, heavier mycelium than was observed with any other compound.

The toxic properties of KOH are probably largely due to the $\bar{O}H$ ion. It is about 94 percent dissociated[1] at $n/12$ its average inhibiting concentration. Just what proportion of the toxic properties is to be attributed to the remaining 6 percent undissociated KOH we have as yet no means of knowing. Inasmuch, however, as KOH is more highly dissociated than HCl at the inhibiting point, and the acid has but $\frac{166}{230}$ of the toxic value of the hydroxide we may safely conclude that the $\bar{O}H$ ion is somewhat more toxic for fungi than ionic $\dot{H}$.

Ammonium Hydroxide, NH_4OH; 29(?) *51*, 83. This compound in contrast with KOH, is but slightly dissociated, $n/40$ the inhibiting strength, being about 8 percent dissociated.[2] The high toxic value is then doubtless due very largely to the unionized molecule. Like KOH, although to a less degree, it caused an excessive development of mycelium in many cultures.

It is worthy of note that *Sterigmatocystis*, which is particularly resistant to both ionic $\dot{H}$ and $\bar{O}H$ is rather susceptible to both acid and hydroxide in the molecular form.

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[1] Ostwald. Jour. prakt. Chem. (2) **33**, 353 (1886).

[2] Kohlrausch. Wied. Ann. **26**, 197 (1885).

These results with hydroxides are not in harmony with those obtained by Krönig and Paul[1] with anthrax spores. They found that the bases KOH, NaOH, LiOH, and NH_4OH "*disinfect in direct proportion to their degree of ionization*", NH_4OH being practically non-toxic. Anthrax spores have evidently a great specific resistance to this agent, and perhaps even a general comparison would be unfair. Be this as it may, ammonia is undoubtedly one of the more violent poisons for mold fungi, far surpassing the mineral acids, copper, cobalt, etc., in toxic properties and comparing favorably with KCN.

Data as to the effect of hydroxides on the higher plants is rather meager. Kahlenberg and True[2] found *Lupinus* could survive in $n/200$ KOH. As it would be practically completely dissociated at this concentration *Lupinus* is evidently much more resistant to $\bar{O}H$ than to ionic $\dot{H}$. Bokorny[3] found that ammonia in $n/689$ concentration in common with other basic substances caused the production of granules in the protoplasm of *Spirogyra* cells, but failed to otherwise modify the normal activities of the cell.

Formaldehyde, HCHO; 0.553, 1.47, 2. Formaldehyde proved to be one of the most deadly agents tested, being surpassed in this respect by mercury, silver, and the two chromates only. Chemically considered, formaldehyde is a very unstable compound intermediate between methyl alcohol and formic acid, being in fact the intermediate step in the oxidation process by means of which the latter is derived from the former. It is both a reducing and oxidizing agent, and this together with its great instability, may account for its intensely toxic properties towards fungi.

To many kinds of protoplasm, including that of the higher animals and perhaps the higher plants, formaldehyde is non-toxic. Instances are on record of persons having drunk a one percent solution without inconvenience.[4] To the lower animals,

[1] Krönig and Paul, loc. cit.
[2] Kahlenberg and True, loc cit. p. 95.
[3] T. Bokorny. Jahrb. f. Wiss. Bot. **19**, 205 (1888).
[4] J. C. Arthur. Bull. of Purdue Univ. Exp. Sta. No. 65, p. 21 (1887).

however, it is more toxic, *n*/60 being fatal to worms, molluscs, and isopods in two hours.[1] Loew and Bokorny[2] found that algae could use a one percent solution for the production of starch. Acton,[3] on the other hand, in experiments on the assimilation of organic compounds by green plants found that while they could use glucose, saccharine, glycerine, etc., *they fail to use aldehydes or their derivatives.* Cohn[4] found one percent solutions very fatal to *Spirogyra.*

For the fungi, however, there is no doubt that in formaldehyde we have one of our safest, most energetic, and serviceable poisons. *n*/512 proved fatal to *Aspergillus* and *Penicillium; n*/2048 to *Sterigmatocystis* and *Botrytis. Œdocephalum* was inhibited by *n*/16384 and killed by *n*/8192. In other words, one part by weight in 273,066 parts of beet infusion proved fatal to *Œdocephalum*, and one part in 4,369,066 permitted the germination of but 10 percent of the spores in eleven hours (as compared with 95 percent in four hours in the checks) and greatly injured the mycelial development. In regard to the other forms, *n*/8192, although greatly retarding germination, caused a distinct stimulation of mycelial development on the second day, the cultures when mature resembling those produced in media containing alcohol.

Very interesting in this connection are the theories regarding the synthesis of starch in the higher plants and of the proteids in the fungi,[5] in both of which formaldehyde has long been regarded as forming a very important step. These theories, particularly that in regard to the synthesis of proteids in the fungi, challenge further careful investigation. It seems, *prima facie*, inconceivable that a compound markedly injurious to a plant when present in the almost infinite dilution of one part by weight in 4,369,000 parts nutrient medium, as in the case of *Œdocephalum*, should be formed by the protoplasm of that plant and be used again in the synthesis of its proteids, as must be the case if our theories be correct.

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[1] O. Loew. Sb. Ges. f. Morphol. u. Physiol. **4,** 39 (1888).
[2] Loew and Bokorny. Jour. prakt. Chem. (2) **36,** 272 (1887).
[3] E. H. Acton. Proc. Roy. Soc. Lond. **46,** 118 (1889).
[4] Bot. Centralblatt, **57,** 5 (1894).
[5] W. M. Klozlowski (quoting Loew, 1880). Bull. Torrey Bot. Club, **26,** 35.

In regard to the nature of its toxic action, it is believed to act upon the propeptones and the albumins, affording compounds which are not readily soluble.[1]

Ethyl Alcohol, $C_2H_5.OH$; 717, *3686*, 8602. Alcohol, as compared with formaldehyde, is apparently non-poisonous. One molecule of formaldehyde has powers of inhibiting the germination of fungus spores equal to those of 2600 molecules of alcohol. The contrast in their killing powers is even greater, being as 1 to 4300. Yet alcohol is a distinct protoplasmic poison to plants, as is well known, being quite extensively used as a fixing agent for tissues. It inhibits germination in the spores used at an average concentration of $n/1.3$ and kills all except *Penicillium* in $4n/1$. Five percent of the spores of *Penicillium* survived immersion in this concentration (17.6 percent) for 72 hours at 28° C. All, however, were killed by $8n/1$ which was the greatest concentration required to kill in the case of any agent tested.

The presence of alcohol in $n/8$ and $n/16$ concentrations distinctly retarded germination of *Sterigmatocystis* and *Botrytis*. No retardation was noticed with *Aspergillus* or *Œdocephalum*. There was indeed some evidence of acceleration in $n/16$ and $n/32$ with *Œdocephalum*, but it is not sufficiently marked to be certainly stated. The mycelial stimulation and retardation of fruiting in $n/4$ was very marked with *Aspergillus* and *Sterigmatocystis*. *Œdocephalum* and *Penicillium* showed some stimulation of mycelial development and a very slight retardation of fruiting. *Botrytis* produced its heaviest mycelium in $n/16$ and $n/32$.

The change which a plant may undergo as it grows older, in the character of its election of foods is of great interest to physiologists.[2] Duclaux[3] found that while alcohol restrains or arrests germination of mold spores, it is made use of almost as abundantly as sugar as a food by the adult plant. My results would seem to support this view. It may be possible, however, that alcohol acts as a stimulant rather than as a food, as is the case with zinc sulfate when present in small quantities. Rich-

[1] C. B. Davenport. loc. cit. p. 20.

[2] C. B. Davenport. loc. cit. **2**, 333 (1899).

[3] Sur la nutrition intracellulaire. Ann. de l'Inst. Pasteur, **3**, 97 (1889).

ards[1] found that the addition of 0.0035 percent $ZnSO_4$ to a culture medium in which *Aspergillus niger* was growing, doubled the dry weight of the mycelium. 0.008 percent $ZnSO_4$ similarly added to a flask culture of *Botrytis* caused a production of quadruple the normal weight of mycelium. We cannot suppose that the small amount of zinc present in itself caused the greater development of supplying nourishment, Zn not being a necessary or desirable element in a nutrient medium for fungi. Richards interpreted the function of the Zn to be that of a *stimulant* rather than a food. May it not be that alcohol performs a similar stimulating function, rather than that it produces an acceleration of growth by nourishment?

Whatever may be the true explanation of the influence of alcohol on the development of the mold fungi, it seems to be demonstrated that the protoplasm of the molds is more sensitive in the conidial stage to the influence of this and many other agents than at any other stage in their development.

Potassium Cyanide, KCN; 2.2, *25.6*, 77. Potassium cyanide in aqueous solution is very unstable. A solution of 24 percent KCN in pure water was prepared by the chemist, and on being used within three hours of titration gave the following critical points with *Aspergillus* and *Penicillium*:

Aspergillus in $n/128$ grew, in $n/16$ failed.
Penicillium in $n/128$ grew, in $n/16$ failed.

Ten days later this stock solution was again tested, it having been kept in a dark cupboard at laboratory temperature in the meantime, with the following result:

Aspergillus in $n/32$ grew, in $n/16$ failed.
Penicillium in $n/64$ grew, in $n/32$ failed.

A solution of beet infusion containing $n/8$ $\overline{CN}$ was then made up from a stock solution and placed in a constant temperature of 28° C for ten days longer, and again tested. The critical points were then as follow:

Aspergillus in $n/16$ grew, in $n/8$ failed.
Penicillium in $n/16$ grew, in $n/8$ failed.

[1] Jahr. f. Wiss. Bot. **30**, 665 (1897).

From these data we learn that a 24 percent aqueous solution of KCN deteriorates so that at the end of 10 days it has but little more than 1/4 its former toxic value. Made up in beet infusion at $n/8$ concentration and kept 10 days longer it retains but 1/8 of its original toxic value. All cultures with KCN reported in this paper, except those noted above, were made up within four hours of preparing the stock solution.

It will be seen by reference to the charts that KCN has almost exactly nine times the toxic effect of ionic $\dot{H}$. KCN in the effective concentrations is quite highly ionized into non-toxic $\dot{K}$ and $\bar{CN}$. To assume that the $\bar{CN}$ radical has nine times the toxic value of $\dot{H}$ would not be justified in view of Shields's[1] studies regarding aqueous solutions of the salt. According to the data worked out by this investigator about 2 percent of KCN would be hydrolyzed in the concentration causing inhibition of the spores, with the formation of a corresponding amount of the deadly HCN. From what we have already learned regarding the toxic properties of this acid, we find that approximately 15 percent of the toxic effect of the KCN is due to the hydrolysis. This would indicate a toxic value for the $\bar{CN}$ ion of something less than 8 $\dot{H}$.

Kahlenberg and True[2] find that towards *Lupinus* it has the value of 1 $\dot{H}$ only. They also show that in the cases of potassium ferro- and ferricyanide the iron and the $\bar{CN}$ radical form complex ions, the toxic value of which is far less than that of the $\bar{CN}$ ion alone.

KCN caused a very marked retardation of germination and early growth in all the forms. Many cultures considerably retarded soon apparently overcame the effect of the poison and grew and fruited normally. *Sterigmatocystis*, in so many cases highly resistant, proved particularly susceptible in this agent.

[1] Shields. loc. cit. (1893).

[2] Kahlenberg and True. loc. cit. 102.

Mercuric Chloride, $HgCl_2$; 0.0258, *0.281*, 0.331. This proved the most fatal compound tested, leading silver nitrate by a very narrow margin.

It is of interest to note here that although only very slightly volatile at ordinary temperatures, and doubtless less so in aqueous solution, mercuric chloride is sufficiently volatile to be distinctly toxic in aqueous solution at 28° C. This was demonstrated by placing a few drops of a very dilute solution in the bottoms of cells containing hanging drops of pure beet infusion inoculated with mold spores. The germination of the spores was inhibited. Mycologists have frequently reported failure to germinate spores in cells which had been sterilized by rinsing in a dilute solution of $HgCl_2$; these failures were doubtless due to the volatile properties of this agent together with its extremely deadly character.

Mercury would appear to be a universal protoplasmic poison. In this as in the less toxic agents, however, the various plants present very great differences in resistance. *n*/65536 proved fatal to *Botrytis*, while a solution containing 16 times this concentration was necessary to prevent development in *Aspergillus* and *Sterigmatocystis*. There would seem, however, to be less difference than with most agents in its relative toxic properties towards the fungi and the higher plants. Kahlenberg and True[1] found *n*/6400 fatal to *Lupinus*, but *n*/12800 permitted growth. The hydroxides, chromates, and formaldehyde were the only other agents tested by the writer which would seem to be more toxic for mold fungi than had been previously determined for the higher plants. To bacteria it is equally fatal, *n*/70000 $HgCl_2$ in nutritive bouillon preventing the development of the splenic fever bacterium.[2]

Silver Nitrate, $AgNO_3$;* 0.0125, *0.375*, 0.375. Almost if not altogether as violent a poison as mercury, silver stands with it at the head of the list of toxic agents. Among the poisons for molds tested, it is comparable with mercury alone among the metals, and with chromate and bichromate anions and formalde-

[1] loc. cit. p. 102 (1896).

[2] C. B. Davenport. loc. cit. I. p. 14 (1897).

hyde only among the other agents. As is the case with bacteria,[1] towards the molds silver is frequently a more violent poison than mercury. Of the five forms used *Œdocephalum* and *Penicillium* proved more susceptible to silver, while *Aspergillus* and *Botrytis* were more susceptible to mercury. The fifth form, *Sterigmatocystis*, had an equal resistance to both. The extraordinarily small quantity of mercury required to kill *Botrytis*, however, left the honors with mercury as the more deadly agent. A very striking contrast in specific resistances is afforded by *Botrytis* and *Penicillium* in solutions of these agents. 1/16 the amount of $HgCl_2$ necessary to kill *Penicillium* was fatal to *Botrytis*. With $AgNO_3$, 1/4 the amount necessary to kill *Botrytis* was fatal to *Penicillium*. In other words, $AgNO_3$ has eight times the toxic value of $HgCl_2$ towards *Penicillium*, while the exact converse is true with *Botrytis*. In general, a smaller amount of Ag caused injury to the mycelium than was required of Hg.

Towards splenic fever bacteria gold is the only other metal comparable in toxic properties with mercury and silver.[1] Towards phanerogams silver is much more toxic than mercury, *n*/102400 being fatal to *Zea*,[2] and *n*/204800 to *Lupinus*.[3]

At the concentrations used the $AgNO_3$ would be practically entirely dissociated.[4]

Cadmium Nitrate, $Cd(NO_3)_2$; 0.075, *6.1*, 24. Ranking closely with silver as a poison for the higher plants, cadmium proves to be very highly toxic to the mold fungi. The most marked feature in the cultures with cadmium was the wide range between the killing point and the point where the development was only noticeably injured. It will be noticed that the ratio of its coefficient of injury to that of $HgCl_2$ is less than 3:1, while the ratio between their death-points is 75:1. A second point worthy of mention is the very great variation in the specific resistances of the different forms. *n*/4096 proved fatal to *Botrytis*, but *n*/32 was required to kill *Sterigmatocystis*. *Penicillium* spores

[1] C. B. Davenport. loc. cit. **1**, 14 (1897).
[2] F. D. Heald. loc. cit. p. 152 (1896).
[3] Kahlenberg and True. loc. cit. p. 104 (1896).
[4] Kohlrausch. Wied. Ann. **26**, 161 (1885).

did not show their usually high relative resistance *n*/256 proving fatal, a solution in which the usually sensitive *Œdocephalum* actually germinated 95 percent and matured a few fruits.

Molisch[1] was one of the first to record the toxic properties of cadmium to plants. He found *n*/33 fatal to *Aspergillus* when experimenting with various elements in an endeavor to find a substitute for calcium in nutrient media. *n*/64 proved fatal to the form of *Aspergillus* used by the writer.

At its average inhibiting concentration cadmium nitrate would be about 90 percent dissociated.[2]

OXIDIZING AGENTS

Potassium dichromate, $K_2Cr_2O_7$; 0.094, *0.3*, 1.25
Potassium chromate, K_2CrO_4; 0.156, *0.4*, 2.25
Hydrogen peroxide, H_2O_2; 38, *105*, 127.0

In general these agents acted similarly. The feature of all three, but more particularly the hydrogen peroxide, was the tendency to bring to fructification every culture which made any considerable mycelial development whatever. With the exception of *Œdocephalum* germination was more or less retarded, particularly in the chromates.

Cultures in *n*/312 H_2O_2 with *Œdocephalum* showed a very marked stimulation of growth from the first sign of germination. At 4 hours after the cultures were inoculated they showed 5 percent more germination than was recorded for the checks at that time. So small a percentage, however, must not be taken as conclusive evidence of acceleration of germination. It will be recalled that a similar observation was made regarding this form in cultures with alcohol. If these were indeed *bona fide* cases of acceleration of germination they are entitled to the honor of being the only ones observed.

The chromates at the dilutions at which they are effective are doubtless practically entirely dissociated.[3] As poisons for molds they rank, as already mentioned, with formaldehyde, sil-

[1] Sitzungsber. Akad. Wiss. Wien. **103**, Abth. 1 (1894).
[2] O. Grotrian. Wied. Ann. **18**, 176 (1883).
[3] Ostwald. Zeit. phys. Chem. **2**, 78 (1888).

ver, and mercury. The anion of the dichromate, $\bar{Cr_2O_7}$, has a toxic value of about 770 ionic $\dot{H}$; that of the chromate 575 $\dot{H}$. This may indicate some relation between their oxidizing powers and their toxicity.

Towards the higher plants these anions would seem to be much less toxic. *Lupinus*[1] survived in a solution of $n/6400$ $K_2Cr_2O_7$ the same concentrationas just permitted growth in the case of the completely dissociated mineral acids. Towards the algae,[2] however, both these anions are strongly toxic, $n/295$ $K_2Cr_2O_7$ being fatal to *Spirogyra* in a few hours. H_2O_2 is a more violent poison to algae[3] than to molds, and ciliata are even more susceptible. Paneth[4] found "0.005 percent" solution to be the limiting line for the latter.

The disinfecting value of H_2O_2 seems to have been greatly overestimated by several workers. Miquel[5] places it as third in toxic properties of all agents used by him, being antiseptic in dilution of one part to 20000. In the same table mercuric chloride and silver nitrate are rated as antiseptic in 1:14300 and 1:12500, respectively. Sternberg[6] found H_2O_2 to have a comparatively low disinfecting value.

Commercial preparations of H_2O_2 vary very greatly in the amount of H_2O_2 in solution. A true 10-volume solution should yield, when fully decomposed, ten volumes of O and contain by weight 3.04 percent H_2O_2. The preparation used in this study, although "fully guaranteed", etc., contained but 2.59 percent H_2O_2 on being tested.

SULPHATES OF THE STRONGLY-TOXIC METALS

These salts are arranged in the order of their toxic properties towards molds in the following list:

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[1] Kahlenberg and True. loc. cit. 1, 107 (1896).
[2] O. Loew. Ein natürliches System der Gift-Wirkungen, p. 16, (1893).
[3] T. Bokorny. Jahrb. f. Wiss. Bot. 17, 347 (1886).
[4] J. Paneth. Centrl. f. Physiol. 3, 377 (1889).
[5] Miquel. Les organismes vivants de l'atmosphere, Paris, (1883).
[6] Manual of Bacteriology, p. 165 (1892).

Nickelous sulphate, $NiSO_4$, 4.8, *33.6*, 1155
Cobaltous sulphate, $CoSO_4$, 6, *57.6*, 389
Ferrous sulphate, $FeSO_4$, 14.4, *115*, 2150
Copper sulphate, $CuSO_4$, 8.4, *131.2*, 582
(Copper nitrate, $Cu(NO_3)_2$, 8.4, *134*, 634)
Zinc sulphate, $ZnSO_4$, 26.4, *602*, 3072

The data as to the dissociation of these sulphates is rather meager. They are, however, not greatly different in dissociation at the same concentrations. This is about 40 percent to 44 percent at *n*/20 concentration.[1]

Nickelous sulphate. The different forms exhibit more variation in their specific resistances to this agent in regard to the death-point than was observed with any other, surpassing that shown in the case of $Cd(NO_3)_2$ considerably. *n*/128 proved fatal to *Botrytis*, while *Aspergillus* failed to lose its vitality in a normal solution (containing over 13 percent anhydrous $NiSO_4$) for 48 hours. As an inhibiting agent, however, it is the most powerful of this group.

Cobaltous sulphate stands in second place, but as will be observed it is distinctly the most *fatal* agent.

Ferrous sulphate. Iron, a necessary element for the nutrition of the molds[2] in common with all other plants, proves to be in excess actually more toxic than that king of modern fungicides, copper.

Copper sulphate and nitrate. These salts proved very similar in toxic properties, as may be noticed by a glance at the diagrams. The nitrate, however, at the critical concentrations is much more highly dissociated than the sulphate. We may judge from this that the un-ionized molecule, $CuSO_4$, has a toxic value not greatly different from ionic Cu^{++}. *Penicillium* although inhibited by *n*/64 $Cu(NO_3)_2$ and *n*/128 (one percent) $CuSO_4$ is not entirely killed by immersion in either concentration for 48 hours.

De Seynes[3] reports growing cultures of *Penicillium glaucum* from different sources, on solutions containing 2–9.5 percent $CuSO_4$. Cultures grown on the latter concentration bore red

[1] See Whetham. loc. cit. pp. 218–276 (1895).
[2] Molisch. loc. cit.
[3] Bull. de la Soc. Bot. de Fr. **42**, I, 451; II, 482 (1895).

conidia. Pfeffer[1] reports finding *Penicillium* growing on a "concentrated solution" of $CuSO_4$. Manasein[2] finds from his experiments that this salt must be present in a 2.5 percent concentration before it has any appreciable affect on this fungus. Here, perhaps, is a hint to plant physiologists of the possibilities yet to be investigated in the acclimatization of fungi (and other plants) to chemical agents.

Zinc sulphate, as will be seen, has a very low toxic value for the molds, whether considered as an inhibiting or killing agent. *Aspergillus* was especially resistant, surviving an immersion in $2n/1$ (27 percent anhydrous $ZnSO_4$) concentration for 48 hours.

Strychnine sulphate, $C_{21}H_{22}N_2O_2.H_2SO_4$. This alkaloid, the only one experimented upon, was dissolved in the slightly acid beet infusion until a saturated solution was obtained. This was found to have a content of 4.31 percent strychnine sulphate. This gives $n/7$ solution, a normal solution of this substance requiring over 30 percent on account of its very large and heavy molecule.

Sterigmatocystis grew and fruited perfectly in this saturated solution, although germination and early development was retarded. *Aspergillus* and *Œdocephalum* also grew and fruited, but the cultures were much behind the checks. *Penicillium* was inhibited by $n/28$ but not killed by the saturated solution. *Botrytis* was also inhibited by $n/28$ and was killed by $n/14$. That the solution used was completely saturated was shown by the appearance of microscopic crystals in some of the hanging-drops which were exposed for a few moments to the air, the evaporation from the culture medium causing some of the strychnine to crystallize out. The fungi, however, continued to thrive in these cultures, their hyphae growing among the crystals.

These results are in harmony with the theory of Loew[3] that the action of alkaloids is chiefly confined to the plasma of the

[1] Pflanzenphysiologie, **2**, 454 (1881).

[2] Noted by O. Loew in Ein natürliches System der Gift-Wirkungen, p. 36 (1893).

[3] O. Loew. loc. cit. p. 85 (1893).

ganglion cells. Fungi and bacteria having no differentiation of nerve protoplasm are practically unharmed by this agent.

Potassium iodide, bromide, and chloride. These salts proved to have a very low toxic value. A complete series of cultures with the five molds was made up with the iodide only. Its coefficients were determined to be 384, *2457*, and 4915: $n/1$ inhibited all except *Aspergillus*; $2n/1$ was fatal to all except *Penicillium*.

As the potassium salts of the halid acids are all quite highly dissociated, an attempt was made to determine the relative toxic properties of the ionic halogen elements. *Aspergillus* and *Œdocephalum* were used. To these molds ionic $\bar{I}$ proved to be doubly toxic as compared with $\bar{Cl}$. $\bar{Br}$ occupied an intermediate position, being very slightly more toxic than ionic $\bar{Cl}$.

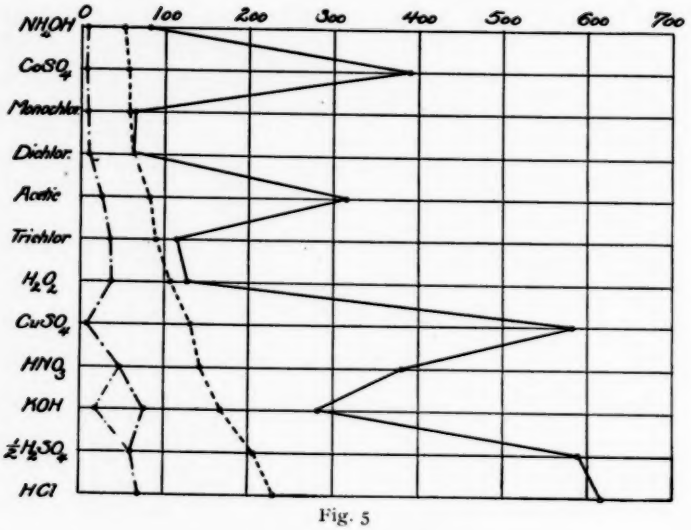
Sodium salicylate $C_6H_4OHCOONa$; 24, *182*, 182. It was thought desirable to test this salt on account of its wide use as a germicide in laboratories and elsewhere. It is, as will be seen, somewhat more toxic than HCl, but not so fatal as HNO_3. *Œdocephalum* was quite susceptible to its influence, $n/128$ being fatal. It is not, however, of much value as a disinfectant, over one percent being necessary to prevent the development of molds.

In the following table the various agents are arranged in the order of the their toxic properties as shown by their powers of inhibiting the germination of the spores of the five species of molds used. The fifth column gives in round numbers the number of molecules of each substance required to produce an inhibiting effect equal to that of *one molecule of mercuric chloride*. The coefficients have as usual the value of x in the expression $x/2048$ of $n/1$.

TABLE III

Agent	Formula	Coefficient of injury	Coefficient of inhibition	Coefficient of death-point	Ratio
Mercuric chloride	$HgCl_2$	.026	.281	.331	1
Potassium bichromate	$K_2Cr_2O_7$	.094	.3	1.25	1.1
Silver nitrate	$AgNO_3$	.013	.375	.375	1.3
Potassium chromate	K_2CrO_4	.156	.4	2.25	1.4
Formaldehyde	$HCHO$	.553	1.43	2	5
Hydrocyanic acid	HCN	.365	3	20	11
Cadmium nitrate	$Cd(NO_3)_2$	.075	6.1	24	22
Potassium cyanide	KCN	2.2	25.6	77	91
Nickelous sulfate	$NiSO_4$	4.8	33.6	1155	120
Ammonium hydroxide	NH_4OH	8	51	83	182
Cobaltous sulfate	$CoSO_4$	6	57.6	389	206
Monochloracetic acid	CH_2ClCO_2H	8.8	58	64	207
Dichloracetic acid	$CHCl_2CO_2H$	10.4	64	64	229
Acetic acid	CH_3CO_2H	25.6	83	314	296
Trichloracetic acid	CCl_3CO_2H	37	90	115	321
Hydrogen peroxide	H_2O_2	38	105	127	375
Ferrous sulfate	$FeSO_4$	14.4	115	2150	411
Copper sulfate	$CuSO_4$	8.4	131	582	468
Copper nitrate	$Cu(NO_3)_2$	8.4	134	634	479
Nitric acid	HNO_3	48	141	384	503
Potassium hydroxide	KOH	$\frac{110}{177}$	166	282	593
Sodium salicylate	$C_6H_4\langle^{OH}_{CO_2Na}$	24	182	182	650
Sulphuric acid	$\frac{1}{2}H_2SO_4$	61	205	589	732
Hydrochloric acid	HCl	70	230	614	821
Zinc sulfate	$ZnSO_4$	26.4	602	3072	2150
Strychnine sulfate	$C_{21}H_{22}N_2O_2{\cdot}H_2SO_4$	179	—	—	—
Potassium iodide	KI	384	2457	4915	8775
Ethyl alcohol	C_2H_5OH	717	3686	8602	13164

Charts 5–7 are simply a graphic representation of the more important features of this table. The values of the abscissae in each case $= x$ in the expression $x/2048$ of a normal solution.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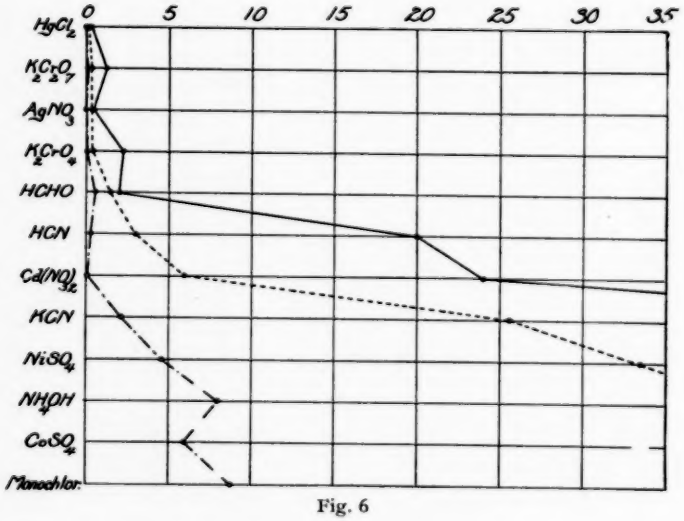
KOH
½H2SO4
HCl

Fig. 5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K2Cr2O7
AgNO3
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HCHO
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Cd(NO3)2
KCN
NiSO4
NH4OH
CoSO4
Monochlor.

Fig. 6

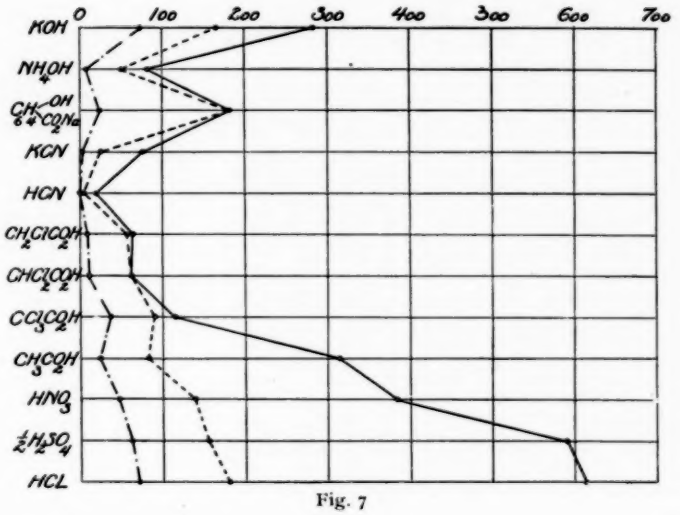

Fig. 7

SUMMARY

1. Fungi are in general much more resistant to most deleterious agents than the higher plants. In the case of the mineral acids a concentration of from two to four hundred times the strength fatal to the higher plants is required to inhibit germination of the spores of molds under favorable conditions for development.

2. Different species of fungi present great differences of resistance to many agents. Of the agents tested in this study, $NiSO_4$ permitted the greatest specific variation and dichloracetic acid the least.

3. Particular forms of the same species present very different powers of resistance, depending probably on previous environment.

4. Individual spores taken from the same pure culture often present considerable variation in resistance.

5. The five forms used were found to be increasingly resistant to the toxic action of the acids in the following order:

Œdocephalum, Botrytis, Penicillium, Aspergillus, and Sterigmatocystis.

6. *Œdocephalum* and *Botrytis*, although on the average the most susceptible to chemical agents of various kinds, have great specific resistances to certain agents. See $FeSO_4$, KI, alcohol, etc.

7. Tests made with media not well suited for the normal development of the fungi tested, will give a correct value for the *killing concentration*, but the data regarding the point of inhibition of germination in such media is not of value.

8. Tests of the toxic value of solutions are unreliable when made in hanging-drop cultures where water was used in the bottom of the cell instead of a solution similar in composition to that forming the hanging-drop. The variation in the toxic value indicated from the actual value will depend on the *vapor pressures* of the solutions used. Volatile — especially highly volatile — and hygroscopic solutions will show the greatest error.

9. Many deleterious agents which at certain concentrations retard germination and early development afterward cause a great acceleration of mycelial development in these cultures. This abnormal growth is ordinarily accompanied by retardation of fruiting.

10. In the conidial stage the protoplasm of molds is in general more sensitive to the action of deleterious agents than at any other stage in their life history.

11. The effect of the different deleterious agents on the appearance of the mycelium is very varied and often quite characteristic.

12. One is not justified in drawing any conclusions as to the killing powers of an agent from its effect in inhibiting the germination of spores.

13. The hydroxyl group $\overline{OH}$ is rather more toxic to molds than ionic $\overset{+}{H}$.

14. The toxic value of the halogens Cl, Br and I in the *ionic* state increases somewhat in the order of increasing atomic weight.

15. The cyanogen radical is a very powerful poison to fungi, KCN having nine times the toxic value of HCl.

16. Mercuric chloride and silver nitrate are about equally toxic to molds, and are followed closely in toxic properties by potassium bichromate, potassium chromate, and formaldehyde.

17. Strychnine and hydrocyanic acid, both extremely powerful poisons to the higher animals, and both supposed to act on the protoplasm of the nerve cells, react very differently towards fungi. To the molds strychnine is practically non-toxic, whereas hydrocyanic acid is a very violent poison.

18. Nickel, cobalt, iron, copper, and zinc inhibit mold spores in the order named. Zinc is much less toxic than the others.

19. That an element is necessary for the nutrition of a plant, does not indicate whether it would or would not be a poison in greater concentration. See iron, oxygen, etc.

20. That an element is not necessary for the normal development of a plant, does not imply that it would be injurious even in relatively great concentration. See chlorine, calcium, etc.

21. The dissociation of the molecule of electrolytes in aqueous solution has a very important bearing in the study of the physiology of poisons. It is of especial value in determining the element or group of elements in a compound to which its toxic properties are to be attributed.

22. In this study no new evidence has been adduced supporting the theory that the chemical activities of a substance are due wholly or chiefly to the dissociated portion.

23. Evidence has been adduced to the effect that in the case of several acids dissociation *lessens* their chemical activity towards the substances involved in the life processes of plants.

24. In the case of the eight acids investigated, six were found to be much more toxic in the molecular form than after dissociation. The toxic properties of these undissociated molecules varied from approximately 2.8 times that of ionic $\overset{+}{H}$ in the case of acetic acid to 76.6 times that of $\overset{+}{H}$ in hydrocyanic acid.

25. The substitution of Cl for H in the acetic acid radical has a double effect. In the first place, it increases the toxicity of the undissociated molecules to a greater or less extent depending on the number of $\overset{+}{H}$ atoms so replaced. In the second place, it increases the dissociation of the acid. The amount of the dissociation is also dependent on the number of H atoms so replaced, being greatest, as are the toxic properties of the whole molecules, when all three H atoms have been replaced by Cl.

26. These two factors to a great extent counterbalance each other. Which has the greater influence in any given solution depends altogether on the concentration, the increased toxicity of the molecules having the predominating influence at the greater concentrations, and the dissociation being more effective at the greater dilutions.

27. At the concentrations inhibiting germination of mold spores mono- and dichloracetic acids are more influenced by the increased toxic properties of the molecule, and trichloracetic by the dissociation. The former in $n/35$ and $n/32$ concentrations are respectively increased in toxicity 40 percent and 30 percent over the original acetic. Trichloracetic acid on the contrary, at $n/22.8$ concentration, suffers a reduction of 10 percent in toxic properties as compared with the original acetic acid.

28. The anions of the mineral acids, HCl, HNO_3, and H_2SO_4, have a low toxic value for fungi, having less than 1/32 that of ionic $\overset{+}{H}$.

In conclusion I beg to acknowledge my indebtedness to Dr. B. M. Duggar, Instructor in Plant Physiology, and Prof. Geo. F. Atkinson, Professor of Botany in Cornell University, for much valuable advice and assistance, and constant encouragement. My best thanks are also due to Prof. W. D. Bancroft, and Mr. A. L. Knisley, of the Chemical Department, for much help and information on the chemical aspects of the work.

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SOME BOILING-POINT CURVES[1]

BY J. K. HAYWOOD

Until recently, but little work has been done on the distillation of perfectly miscible liquids. In general, the problem has been attacked by measuring the vapor-pressure with varying composition, the temperature being kept constant. In this manner the characteristic phenomena were very completely determined by the work principally of Konowaloff,[2] the researches of Roscoe[3] on solutions of halid acids in water being also important in this connection. But very few pairs, however, have been studied of even the more common liquids.

The investigation here recorded was undertaken to add to our knowledge of the properties of such liquids themselves and in the hope that accumulated data will make possible a clearer insight into the nature of the phenomena presented. Instead of measuring the vapor pressures with constant temperature it would appear to be more profitable to adopt the procedure more nearly like the conditions of actual practice. Therefore, as has recently been done by Thayer,[4] the variation of the boiling-point with composition under constant pressure has been studied. The apparatus used was essentially that of Orndorff and Cameron.[5] The thermometer was graduated to one-tenth (0.1°) and one-fiftieth could be readily estimated, but in general no attempt to read closer than one-tenth seemed to be warrantable. The thermometer had previously been carefully calibrated and no appreciable error could be occasioned from any inaccuracy of the instrument. All readings here given are uncorrected.

The materials employed were all carefully purified and in

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[1] Contribution from the Chemical Division, U. S. Department of Agriculture.

[2] Wied. Ann. **14,** 34 (1881).

[3] Liebig's Annalen, **112,** 327 (1859); **116,** 203 (1860).

[4] Jour. Phys. Chem. **2,** 382 (1898); **3,** 36 (1899).

[5] Am. Chem. Jour. **17,** 57 (1895).

every case, before using, distilled through a high column still; first and last portions being discarded. In no case did the variation in the boiling-point of the purified material amount to more than 0.5° C and seldom to more than 0.1° C. The alcohol was distilled from lime in the conventional way and afterwards from anhydrous copper sulfate. The methyl alcohol after long standing over anhydrous copper sulfate was decanted and distilled. The acetone was long treated with calcium chlorid, filtered and distilled. The chloroform was washed with water four times to get rid of traces of alcohol, carefully dried over calcium chlorid, filtered and distilled. With the carbon tetrachlorid no treatment was found necessary other than the careful distillation through a high column.

All the determinations were made at the prevailing atmospheric pressure, and the corresponding barometric readings are given. In no case was the variation large enough to seriously affect the value of the experiments. It is of course to be regretted, for purposes of comparison, that these pressures could not be the same in all cases, but no great difficulty arises from this cause. The tabulated results follow:

TABLE I

Alcohol and water

% Alcohol	Temp	Bar	% Alcohol	Temp	Bar
100.0	78.2°	751.2	42.5	82.35°	754.5
85.8	78.4	751.4	37.4	83.0	754.1
75.1	79.2	751.7	30.9	83.9	754.0
62.6	80.35	751.8	24.4	85.4	753.8
54.7	80.9	752.0	22.2	85.9	753.5
51.2	81.5	752.1	18.2	87.3	753.3
47.7	81.8	752.3	00.0	99.2	753.1
45.1	82.1	754.8			

TABLE II

Alcohol and ether

% Alcohol	Temp	Bar	% Alcohol	Temp	Bar
100.0	79.0°	772.1	49.2	45.7°	771.4
86.4	67.5	772.1	43.1	43.95	771.4
74.8	58.5	772.0	36.4	42.3	771.3
64.0	54.2	772.0	25.1	39.9	771.3
57.5	49.5	771.8	11.8	37.5	771.3
54.3	47.3	771.4	00.0	35.05	771.3

TABLE III

Alcohol and carbon tetrachlorid

% Alcohol	Temp	Bar	% Alcohol	Temp	Bar
100.0	78.9°	768.8	28.1	65.8°	768.2
87.7	75.85	768.8	20.4	65.55	768.3
73.1	72.4	769.0	17.3	65.5	768.4
57.8	69.4	768.9	11.4	65.6	768.4
50.7	68.2	768.9	8.9	65.8	768.0
46.7	67.6	768.9	5.3	66.5	767.9
45.9	67.5	768.3	2.5	68.5	768.4
39.8	66.8	768.4	0.0	77.2	767.7
34.1	66.225	768.3			

TABLE IV

Chloroform and carbon tetrachlorid

% $CHCl_3$	Temp	Bar	% $CHCl_3$	Temp	Bar
100.1	61.5°	758.4	47.5	66.6°	756.8
92.2	62.0	758.1	42.7	67.25	756.8
79.9	63.1	758.1	38.3	68.0	756.9
70.4	63.95	757.9	29.7	69.45	757.0
62.3	64.8	757.6	20.5	71.3	757.0
56.2	65.5	757.4	9.3	74.1	757.0
50.9	66.2	757.5	0.0	76.75	757.2
49.4	66.4	757.5			

TABLE V

Chloroform and methyl alcohol

% $CHCl_3$	Temp	Bar	% $CHCl_3$	Temp	Bar
100.0	61.95°	770.2	68.4	55.3°	770.4
97.7	56.4	770.2	62.8	56.05	770.3
95.5	54.9	770.2	57.0	56.85	770.3
93.9	54.5	770.2	51.1	57.75	770.2
92.7	54.3	770.2	52.2	57.5	769.8
89.4	54.1	770.2	43.7	58.9	769.8
87.7	54.025	770.2	39.3	59.6	769.8
84.6	54.1	770.4	25.0	61.85	770.0
81.9	54.2	770.4	12.8	63.6	770.0
74.5	54.7	770.4	0.0	65.25	770.0

TABLE VI

Acetone and water

% Acetone	Temp	Bar	% Acetone	Temp	Bar
100.0	56.9°	772.5	45.2	64.5°	772.8
88.2	59.1	772.6	40.5	65.3	772.8
76.4	60.7	772.6	33.4	67.0	772.8
68.5	61.6	772.6	24.3	70.7	772.9
60.0	62.4	772.6	18.4	74.3	773.0
54.1	63.1	772.6	11.1	81.1	773.0
46.4	64.2	773.0	0.00	99.8	772.8

TABLE VII

Acetone and methyl alcohol

% Acetone	Temp	Bar	% Acetone	Temp	Bar
100.0	56.65°	764.5	47.5	58.5°	765.2
88.3	55.85	764.3	43.9	58.8	765.2
83.4	55.9	764.3	38.2	59.5	765.3
75.9	56.1	764.4	32.1	60.2	765.3
65.7	56.65	764.5	20.9	61.8	765.3
57.1	57.3	764.5	7.9	63.9	765.3
51.8	57.75	764.6	0.0	65.2	765.3
49.7	58.0	764.6			

In order to demonstrate more clearly the existence of a minimum point, the following determinations were carefully made:

% Acetone	Temp	Bar	% Acetone	Temp	Bar
100.0	56.7°	765.0	88.2	55.9°	764.8
97.2	56.4	765.0	85.5	55.95	765.1
92.9	56.1	765.0			

Table VIII

Acetone and ether

% Acetone	Temp	Bar	% Acetone	Temp	Bar
100.0	56.75°	768.2	50.3	40.3°	769.2
84.4	48.8	768.1	44.8	39.4	769.2
71.7	45.3	768.1	37.3	38.22	769.3
65.1	43.5	768.0	26.8	36.9	769.4
57.1	41.7	767.9	17.6	36.0	769.5
53 9	41.0	767.9	00.0	35.0	769.5
53.8	40.95	769.1			

TABLE IX

Acetone and carbon tetrachlorid

% Acetone	Temp	Bar	% Acetone	Temp	Bar
100.0	57.0°	773.0	38.6	58.25°	772.5
83.9	56.95	773.0	32.3	58.8	772.5
74.7	57.0	773.1	24.9	59.8	772.5
64.8	57 125	773.1	15.8	61.85	772.6
56.4	57.3	773.0	9.6	64.55	772.6
50.0	57.55	773.0	5.9	67.3	772.7
45.4	57.8	773.0	2.5	72.15	772.7
44.0	57.9	772.5	0.0	77.3	772.8

The existence of a minimum point on this curve was more accurately determined by the following series, in which a Beckmann differential thermometer was used on account of the large scale available in that instrument.

% Acetone	Temp	Bar	% Acetone	Temp	Bar
100.0	2.67°	772.6	71.1	2.67°	772.7
91.3	2.63	772.7	62.3	2.82	772.7
81.0	2.62	772.7	58.1	2.93	772.6

The significance of these results is more readily seen by reference to the accompanying charts. The temperatures are plotted as ordinates, and the percentage compositions by weight are taken as abscissas. No essential advantage is to be obtained by calculating the composition in relative number of reacting weights, the curves being merely displaced to the side and the charts losing in clearness. For purposes of comparison the results of Thayer are included.

In Fig. 1 the results for mixtures of the various liquids with alcohol are given. The curve for water needs no comment, as its general properties were known from the work of Konowaloff. For the sake of completeness it was deemed worth while however to present these results. A practical application, in determining the composition of dilute solutions of alcohol by their boiling-points, appears worthy of consideration in this connection. The curve well illustrates the difficulty in fractioning alcohol with relatively small quantities of water. With chloroform and carbon tetrachlorid respectively very similar results

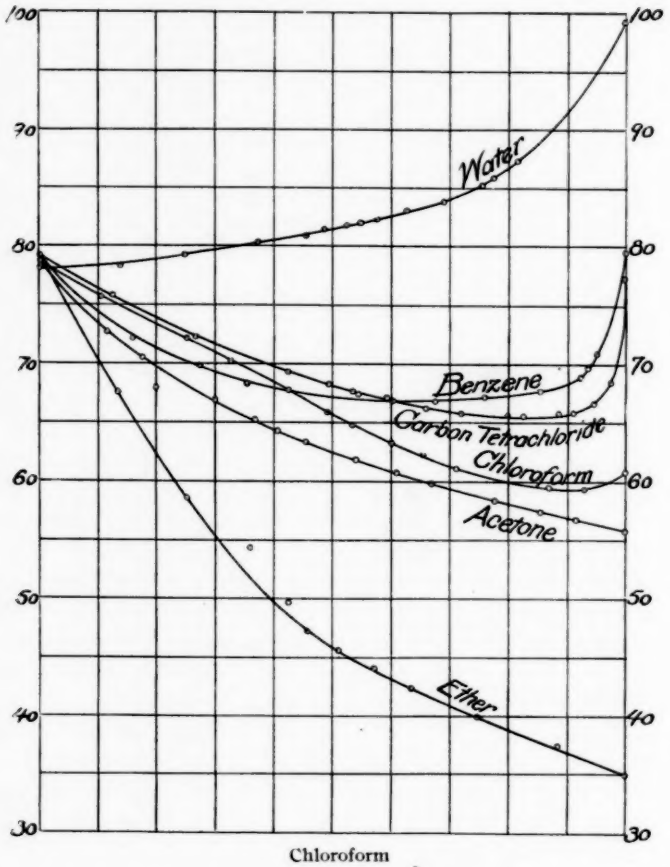

Fig. 1

were obtained. Both curves show a minimum point. In the case of carbon tetrachlorid the mixture with constant boiling-point contains about 17.5 percent alcohol and boils at about 65.5° C under a pressure of 768.4 mm. mercury. The slight waviness noticed by Thayer at the alcohol end of the curve for chloroform does not appear in the case of carbon tetrachlorid. In fact, if both curves had been determined at the

same pressure it seems evident that the chloroform one would rise slightly then fall again until at about a composition of 35 percent chloroform it would cut the curve for carbon tetrachlorid and from this point on the two curves diverge fairly rapidly. The curves for acetone and ether respectively present no unusual features and require no further comment.

An experimental point of importance is to allow the contents of the apparatus to cool well before adding successive portions of ether. My results here charted indicate the importance of this precaution, two of the boiling-points being obviously too high, probably on account of some of the material being lost by the violent ebullition resulting from adding the ether to the hot alcoholic solution.

In Fig. 2 are plotted the curves for mixtures in which

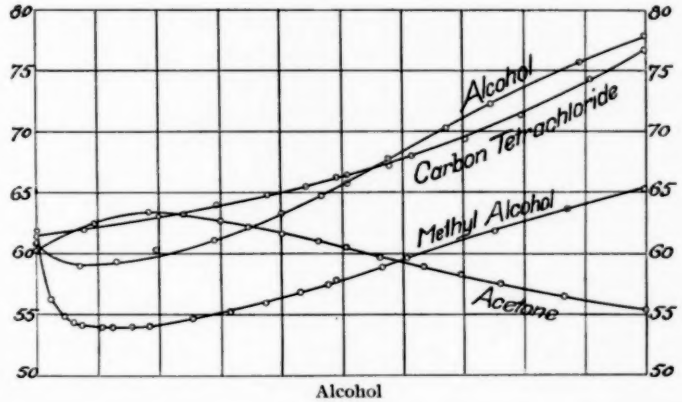

Fig. 2

chloroform is one constituent. With carbon tetrachlorid the curve obtained has neither a maximum nor minimum point, and presents no remarkable features. The curve for methyl alcohol is very similar in general features to the one for ethyl alcohol. It shows a minimum point corresponding to a mixture containing about 87.5 percent chloroform and boiling at 54° C under a pressure of 770.2 mm of mercury. The waviness at the methyl alcohol end of the curve is quite as marked as in the case of

ethyl alcohol. Indeed this waviness would appear to be a general characteristic for curves corresponding to chloroform solutions.

Fig. 3 illustrates the results obtained for solutions in which

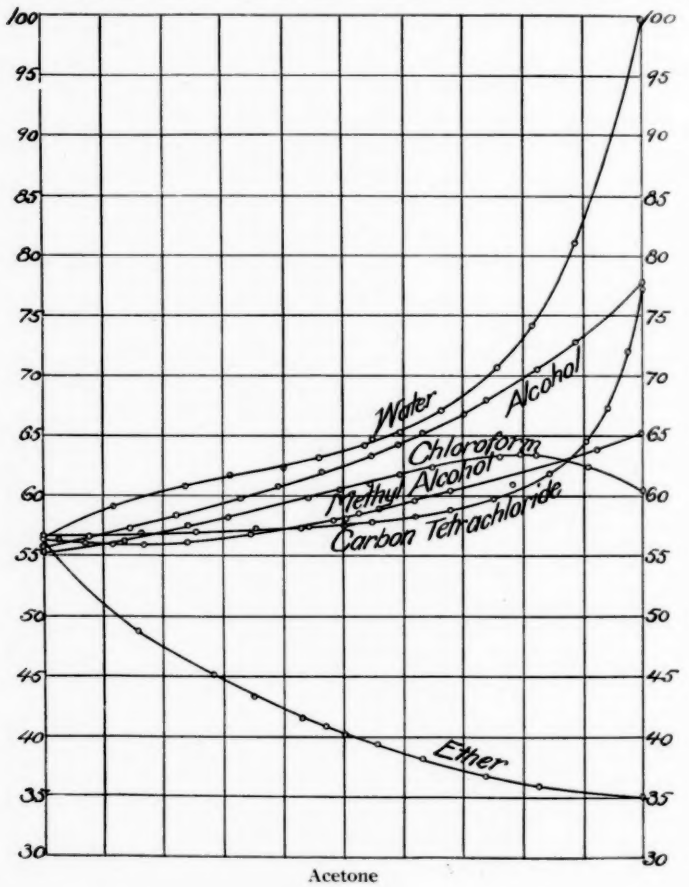

Fig. 3

acetone is a constituent. The curve for water is peculiarly interesting on account of the well-marked wavy character it presents. It would appear that if the pressures had been the same

the alcohol and water curves respectively would have intersected in two points. Up to mixtures containing about 30 percent of acetone the two curves lie very close together. No maximum or minimum point is shown. The curve for ether shows no special features. The curve for methyl alcohol, as it appears on the chart, is very similar to that for ethyl alcohol. It, however, has a true minimum point corresponding to 87 or 88 percent acetone, and a boiling-point of about 55.9° C at a pressure of 765 mm of mercury. In other words, the boiling-point of the constant boiling solution is only about 0.8° below that of the pure solvent. It is fortunate, in view of this fact, that we are not dependent upon fractional distillation for a separation of these substances.

The curve for carbon tetrachlorid is even more striking. It does not in the least resemble that for chloroform. All mixtures down to about 35 percent of acetone have practically the same boiling-point as the pure solvent, and further the case is complicated by the existence of a true minimum point, as was shown by careful experiments, corresponding to a concentration of 80 to 85 percent acetone and with a boiling-point only about 0.05° below that of the pure solvent. The curves for methyl alcohol and carbon tetrachlorid respectively lie strikingly near each other for solutions down to about 12 percent of acetone, and intersect each other twice. A curious coincidence is the intersection of the three curves for methyl alcohol, carbon tetrachlorid, and chloroform respectively at practically the same point.

From the cases so far studied certain generalities are indicated, though the number of cases is hardly sufficient to justify more than tentative statements. It would seem that the existence of a maximum or a minimum point is more probable when the boiling-points of the constituents themselves lie near one another. The case of carbon tetrachlorid and chloroform immediately suggests itself as an exception, but the fact of the close chemical relationship of these two compounds may very readily be a strong modifying influence. From the results of Lehfeldt,[1]

[1] Phil. Mag. [5] **46**, 42 (1898).

it would appear that the curve for carbon tetrachlorid and benzene is also an exception, but it cannot be admitted that the nature of this curve is established, on account of the very few observations upon which it was plotted, and it is not unlikely that further work will bring this case into line.

With the same solvent, substances of a similar chemical nature apparently yield similar curves. One well marked exception appears: carbon tetrachlorid and chloroform in acetone, for which no explanation is at present obvious.

For counsel and assistance in the investigation here presented, I am indebted to Dr. Frank K. Cameron.

At an early date I hope to present the results of observations upon solutions in benzene, methyl alcohol and other solvents.

From the facts here presented the following conclusions may be drawn:

1. All mixtures of the following pairs of liquids boil at temperatures between the boiling-points of the constituents: alcohol-water, alcohol-ether, chloroform-carbon tetrachlorid, acetone-water, and acetone-ether.

2. A solution containing 17.5 percent alcohol in carbon tetrachlorid, distills without a change at 65.5° C, approximately, under a pressure of 768.4 mm of mercury.

3. A solution containing 12.5 percent methyl alcohol in chloroform distills without change at 54° C, approximately, under a pressure of 770.2 mm of mercury.

4. A solution containing 12 to 13 percent of methyl alcohol in acetone distills without change at 55.9° C, approximately, under a pressure of 764.8 mm of mercury.

5. A solution containing 15 to 20 percent of carbon tetrachlorid in acetone distills without change at a temperature but 0.05° below that of the pure acetone, and all mixtures containing more than 40 percent of acetone boil within one degree of the boiling-point of the acetone itself.

6. The close proximity of the boiling-points of the con-

stituents appears to be a favorable condition for the existence of a maximum or a minimum point on the boiling-point curve. Similarity of constitution seems to be a strongly modifying condition however.

7. In general, one constituent remaining the same, mixtures with substances of similar chemical constitution yield similar boiling-point curves.

THE DELIQUESCENCE OF POTASSIUM NITRATE, SODIUM NITRATE, AND AMMONIUM NITRATE

BY F. L. KORTRIGHT

In spite of the fact that the nitrates of potassium, sodium, and ammonium are largely used in the manufacture of explosives and on that account an accurate knowledge of their deliquescence is desirable, I have not been able to find any such information in the literature. No less an authority than Professor Lunge,[1] in speaking of the solutions from the lixiviation of the bags in which Chili saltpeter has been imported, says: "The solution is evaporated to a small bulk and crystallized. The mother-liquor from this operation is always very rich in chlorides, which seems to show that the deliquescence of sodium nitrate is not a property of the pure salt, but is owing to the magnesium chloride and calcium chloride contained in it, since the dampest salt still adheres to the bags." And statements like the following appear in the handbooks:[2] "Sodium nitrate is hygroscopic, according to Brandes deliquesces in moist air completely," and[3] "Potassium nitrate absorbs water slowly from the air; 100 parts in the presence of water at 14–22° C in 22 days absorbed 339 parts of water. Small quantities deliquesce." Such statements as these last, while not incorrect, have no value. For the percentage of moisture which the air must contain before it may be called moist is certainly a matter of opinion and any soluble salt will absorb water more or less rapidly, if placed over water.

The trouble seems to be in the lack of an appreciation of the condition that leads to the deliquescence of a salt, and,

[1] Sulphuric Acid and Alkali, 2d Ed., Vol. I, p. 82.

[2] Dammer. Handbuch der anorganischen Chemie, 2_2, p. 196.

[3] loc. cit. 2_2, p. 75.

although this condition is a natural consequence of long known physical laws and has been stated plainly in at least one other place,[1] the apparent ignorance concerning it will justify a restatement in this place.

A salt is deliquescent when the pressure of the water vapor from its saturated solution is less than the partial pressure of the water vapor in the surrounding air, and only then. Understanding this, we at once have a means for accurately determining the conditions under which a salt will deliquesce, for a determination of the vapor-pressure of its saturated solution gives the information desired. I have, therefore, thought it worth while to make these determinations for these three more common and important nitrates.

The sodium nitrate used in these experiments was kindly furnished me by Dr. A. E. Taylor, and was very pure, being a portion of the material[2] which he prepared for his work on "Precipitation of Salts."

The potassium nitrate was from Bender and Hobein and was marked Ph. III.

Both of these salts were finely pulverized and then dried in the air-bath at 145–150° for five hours.

The ammonium nitrate was the purest at hand in the University store-room and showed no tests for the ordinary impurities. This was finely pulverized and dried for seven hours at 100–110° C in the air-bath. Fearing that the prolonged drying had caused a partial decomposition into the nitrites, the salts were tested by Glosway's modification of Griess's method, using sulphanilic acid and *α*-amido-naphthaline acetate. The sodium and potassium nitrates showed no sign of any such decomposition and the ammonium nitrate only contained a trace of the nitrite.

In practice it was found easier to determine directly the partial pressure of the water vapor in the air in which the salt would first deliquesce instead of determining the vapor-pressure

[1] Bancroft. The Phase Rule, 51.

[2] Jour. Phys. Chem. 1, 718 (1897).

of the saturated solution of the salt in question. This was done by preparing desiccators with sulphuric acid solutions of known composition and vapor-pressure.[1] Table I shows the vapor-pressure of the acid solutions used.

TABLE I

	Vap. press		Vap. press
$H_2SO_4 + H_2O$	0.15	$H_2SO_4 + 9H_2O$	10.83
$H_2SO_4 + 2H_2O$	0.85	$H_2SO_4 + 11H_2O$	12.32
$H_2SO_4 + 3H_2O$	2.24	$H_2SO_4 + 14H_2O$	13.50
$H_2SO_4 + 4H_2O$	3.73	$H_2SO_4 + 17H_2O$	14.48
$H_2SO_4 + 5H_2O$	5.79	$H_2SO_4 + 25H_2O$	15.55
$H_2SO_4 + 7H_2O$	8.49	$H_2SO_4 + 50H_2O$	16.55
		Pure H_2O	17.40

The column marked vap. press. gives the vapor-pressure of the solution opposite, in mm of mercury, at 20° C.

These acid solutions were made from acid marked C. P., but containing considerable lead sulphate and fairly free from other impurities. The strength of the acid was determined by weighing out portions in glass-stoppered weighing tubes, dissolving in water and titrating with a carefully standardized $n/5$ normal solution of potassium hydroxide. The mean of three closely agreeing determinations gave 93.42 percent as the strength in sulphuric acid (H_2SO_4). The amount of water necessary for the desired strength of solution was then weighed off and added to the proper amount of acid. Care was taken in mixing to constantly keep the solution cool so as to avoid loss of water through evaporation and the acid was kept carefully covered to prevent gain of water by absorption. The acid solutions were then placed in ordinary six-inch desiccators and over them were placed the nitrates, about three grams on two inch watch-glasses which had already stood in the desiccator 24 hours to come to equilibrium. No particular effort was made to keep the desiccator at a constant temperature, for it was assumed that, for the small variations of temperature which they would undergo in the laboratory, the variations in the vapor-pressures of the acid

[1] These values are mostly from Regnault. Ann. Chim. Phys. (3) **15**, 179 (1845). The vapor-pressure of $H_2SO_4 + 50H_2O$ is from R. v. Helmholtz. Wied. Ann. **27**, 534 (1886), and $H_2SO_4 + 14H_2O$ and $+ 25H_2O$ are interpolation values.

and salt solutions would be in the same direction and nearly equal, so that the comparative result would not be effected by the temperature change, and this assumption was justified by the fact that although the observations extended over several weeks the results remained constant.

Table II shows the result of these observations, n. c. indicates "no change" and means that no change in weight occurred in those cases, although several weighings were made in each case.

TABLE II

H_2SO_4 +

	H_2O	$2H_2O$	$3H_2O$	$4H_2O$	$5H_2O$	$7H_2O$	$9H_2O$
KNO_3	nc	nc	nc	nc	nc	nc	nc
$NaNO_3$	nc	nc	nc	nc	nc	nc	nc
NH_4NO_3	nc	nc	nc	nc	nc	nc	Deliq

	$11H_2O$	$14H_2O$	$17H_2O$	$25H_2O$	$50H_2O$	Pure H_2O
KNO_3	nc	nc	nc	nc	Deliq	—
$NaNO_3$	nc	Deliq	—	—	—	—
NH_4NO_3	—	—	—	—	—	—

From this table one sees that the deliquescence begins as soon as a certain vapor-pressure is reached and only then and further it may be seen that these particular salts are not hygroscopic. This fact was strikingly shown by a three gram sample of sodium nitrate which weighed with glass 8.1488 grams and became wet over $H_2SO_4 + 17H_2O$. It was then removed from the desiccator and left for 24 hours protected from dust and exposed to the atmosphere of a steam heated room, at the end of the 24 hours it weighed 8.1490 grams.

It may then be considered demonstrated that at 20° C ammonium nitrate will deliquesce when the partial pressure of the water vapor in the air is equal to, or greater than, 10.8 mm of mercury and will not deliquesce when this pressure is equal to, or less than, 8.5 mm of mercury, the exact point where deliquescence begins is probably about a mean of these values; with sodium nitrate the deliquescence point lies between 12.3 and 13.5 mm of mercury, and for potassium nitrate it is between 15.5

and 16.5 mm. of mercury and probably more near the upper value.

It has been shown by Emden[1] that even with highly concentrated salt solutions the relative vapor-pressure lowering is proportional to the concentration and independent of the temperature. This may be expressed by the equation

$$s\mu = \frac{P - p}{P}$$

where s is the salt content in grams per 100 grams water, μ is the proportionality constant, P the vapor-pressure of water, and p the vapor-pressure of the salt solution. Solving for p we have

$$p = P - Ps\mu.$$

Therefore knowing P, s and μ we can determine p. That is, we can determine the condition for the deliquescence of that salt. P and s may be obtained from well known tables, and μ may be sufficiently accurately estimated from Emden's results. The value of μ for various values of s, for sodium nitrate and for potassium nitrate, are given in Table III.

TABLE III

$NaNO_3$		KNO_3	
s	μ	s	μ
19.68	0.00373	10.04	0.00308
41.75	0.00349	14.88	0.00291
60.10	0.00330	20.07	0.00279
79.87	0.00312	25.01	0.00268

A glance at these values will show that μ for sodium nitrate varies about 0.00001 for each gram change of concentration and for potassium nitrate about 0.000023, so that taking the μ for a concentration most near to the concentration of the saturated solution we can easily interpolate a sufficiently accurate value for the μ of our saturated solution.

Calculating p by the above formula we have Tables IV and V, in which the various letters have the significance already assigned to them. p is therefore, the vapor-pressure of the saturated solutions of sodium nitrate and of potassium nitrate, at the

[1] Wied. Ann. **31**, 167 (1887).

different temperatures. That is, p shows the partial pressure that the water vapor in the air must have before the salt will deliquesce at the temperature stated.

TABLE IV

$NaNO_3$

Temp	s	μ	P	p
0° C	72.9	0.00319	4.6	3.5
10	80 9	0.00311	9.17	6.9
20	87.5	0.00305	17.39	12.8
30	94.9	0.00299	31.55	22.6
40	102.0	0.00292	54.90	38.1

TABLE V

KNO_3

Temp	s	μ	P	p
0° C	13.3	0.00295	4.6	4.4
10	21.1	0.00277	9.17	8.7
20	31.2	0.00255	17.39	16.0
30	44.5	0.00230	31.55	28.3

The vapor-pressure of the two salts at 20° C calculated in this way agrees with the values experimentally found.

I have thus shown the definite conditions under which the salts considered will deliquesce. The explanation of the concentration of the magnesium chloride in the lower part of the pile of Chili saltpeter is a simple matter, if we consider that the saturated solution of magnesium chloride has a much lower vapor-pressure than that of sodium nitrate. The magnesium salt will, therefore, deliquesce at a lower partial pressure of water vapor in the atmosphere than the sodium nitrate and will thus be dissolved out from the mixture.

Cornell University, March, 1899

ON THE STABILITY OF EQUILIBRIUM OF A ONE-COMPONENT SYSTEM

BY PAUL SAUREL

A one-component system may consist of one, two, or three phases, and the energy ϵ_i of the unit of mass of the i-th phase is a function of the entropy η_i and the volume v_i of the unit mass. If we denote the energy of the system by E, and the mass of the i-th phase by M_i, we may write

$$E = \sum_{i=1}^{r} M_i \epsilon_i, \qquad r = 1, 2, \text{ or } 3.$$

For any virtual change in the system we shall have

$$\delta E = \sum_{i=1}^{r} M_i \delta \epsilon_i + \sum_{i=1}^{r} \epsilon_i \delta M_i,$$

or, since ϵ_i is a function of η_i and v_i,

$$\delta E = \sum_{i=1}^{r} M_i \left(\frac{\partial \epsilon_i}{\partial \eta_i} \delta \eta_i + \frac{\partial \epsilon_i}{\partial v_i} \delta v_i \right)$$

$$+ \tfrac{1}{2} \sum_{i=1}^{r} M_i \left(\frac{\partial^2 \epsilon_i}{\partial \eta_i^2} \delta \eta_i^2 + 2 \frac{\partial^2 \epsilon_i}{\partial \eta_i \partial v_i} \delta \eta_i \delta v_i + \frac{\partial^2 \epsilon_i}{\partial v_i^2} \delta v_i^2 \right) + \sum_{i=1}^{r} \epsilon_i \delta M_i.$$

But, if t and p denote the temperature and the pressure of the system, the conditions of equilibrium are

$$\frac{\partial \epsilon_i}{\partial \eta_i} = \frac{\partial \epsilon_r}{\partial \eta_r} = t, \quad \frac{\partial \epsilon_i}{\partial v_i} = \frac{\partial \epsilon_r}{\partial v_r} = -p,$$

$$\epsilon_i - t\eta_i + pv_i = \epsilon_r - t\eta_r + pv_r.$$

Making use of the first two conditions, we may write

$$\delta E = t \sum_{i=1}^{r} M_i \delta \eta_i - p \sum_{i=1}^{r} M_i \delta v_i + \sum_{i=1}^{r} \epsilon_i \delta M_i$$

$$+ \tfrac{1}{2} \sum_{i=1}^{r} M_i \left(\frac{\partial^2 \epsilon_i}{\partial \eta_i^2} \delta \eta_i^2 + 2 \frac{\partial^2 \epsilon_i}{\partial \eta_i \partial v_i} \delta \eta_i \delta v_i + \frac{\partial^2 \epsilon_i}{\partial v_i^2} \delta v_i^2 \right).$$

Moreover, if the entropy, volume, and mass of the system be denoted by H, V, M, we have

$$H = \sum_{i=1}^{r} M_i \eta_i, \quad V = \sum_{i=1}^{r} M_i v_i, \quad M = \sum_{i=1}^{r} M_i,$$

and

$$\delta H = \sum_{i=1}^{r} M_i \delta\eta_i + \sum_{i=1}^{r} \eta_i \delta M_i, \quad \delta V = \sum_{i=1}^{r} M_i \delta v_i + \sum_{i=1}^{r} v_i \delta M_i, \quad \delta M = \sum_{i=1}^{r} \delta M_i.$$

Making use of these relations and of the last of the conditions of equilibrium we easily obtain

$$\delta E = t\delta H - p\delta V + (\epsilon_r - t\eta_r + pv_r)\delta M + \tfrac{1}{2}\sum_{i=1}^{r} M_i \left(\frac{\partial^2 \epsilon_i}{\partial \eta_i^2} \delta\eta_i^2 + 2 \frac{\partial^2 \epsilon_i}{\partial \eta_i \partial v_i} \delta\eta_i \delta v_i + \frac{\partial^2 \epsilon_i}{\partial v_i^2} \delta v_i^2 \right).$$

The condition for stable equilibrium is that for any virtual change in which the entropy, volume, and mass remain constant, the energy increases. That is to say, if

$$\delta H = 0, \quad \delta V = 0, \quad \delta M = 0,$$

we should have

$$\delta E > 0.$$

The condition for stable equilibrium is, accordingly,

$$\sum_{i=1}^{r} M_i \left(\frac{\partial^2 \epsilon_i}{\partial \eta_i^2} \delta\eta_i^2 + 2 \frac{\partial^2 \epsilon_i}{\partial \eta_i \partial v_i} \delta\eta_i \delta v_i + \frac{\partial^2 \epsilon_i}{\partial v_i^2} \delta v_i^2 \right) > 0.$$

Let us consider first a system containing three phases, an invariant system. In such a system the values of the inner variables η_i, v_i are fixed, but the masses of two of the phases may be taken arbitrarily. In the above expression we may accordingly take two of the masses so small that the term containing the third mass gives its sign to the whole expression. Accordingly, the coefficient of each of the M's must be positive.

Suppose next that the system is in two phases. In such a univariant system, for given values of the inner variables, the mass of one phase is still arbitrary. We may therefore take one of the two masses so small that the term containing the other

gives its sign to the whole expression. As before, the coefficient of each of the M's must be positive.

Obviously, when the system contains but one phase we get the same condition as before. Thus, we must have

$$\frac{\partial^2 \epsilon_i}{\partial \eta_i^2}\,\delta\eta_i^2 + 2\,\frac{\partial^2 \epsilon_i}{\partial \eta_i \partial v_i}\,\delta\eta_i \delta v_i + \frac{\partial^2 \epsilon_i}{\partial v_i^2}\,\delta v_i^2 > 0\,;$$

and the familiar conditions for this are

$$\frac{\partial^2 \epsilon_i}{\partial \eta_i^2} > 0$$

$$\begin{vmatrix} \dfrac{\partial^2 \epsilon_i}{\partial \eta_i^2} & \dfrac{\partial^2 \epsilon_i}{\partial \eta_i \partial v_i} \\ \dfrac{\partial^2 \epsilon_i}{\partial \eta_i \partial v_i} & \dfrac{\partial^2 \epsilon_i}{\partial v_i^2} \end{vmatrix} > 0.$$

If we make use of Gibbs's ϵ-η-v diagram, and if we state in geometrical terms the conditions that we have obtained, we get at once the following theorem, which is due to Gibbs.[1]

In order that the equilibrium of the one-component system should be stable, it is necessary that at the points of the primitive energy surface which represent the coexisting states, the surface should be convex in all directions and this convexity (the ϵ-axis being drawn upward) should be turned downward.

Université de Bordeaux, May, 1899

[1] Gibbs. A Method of Geometrical Representation of the Thermodynamic Properties of Substances by Means of Surfaces. Trans. Conn. Acad. 2, 390 (1873).

NEW BOOKS

Theoretische Chemie vom Standpunkte der Avogadro'schen Regel und der Thermodynamik. *By Walther Nernst. Second Editon. 16 × 25 cm ; pp. xvi and 703. Stuttgart : Ferdinand Enke, 1898.* — The old classification has been followed practically without change, the only alterations being the insertion of a chapter on metals and metallic alloys and the splitting up of electrochemistry into three chapters. The particular arrangement adopted here was interesting in the first edition as a brave though somewhat unsuccessful attempt to present the whole field of physical chemistry in a logical manner in one volume. One serious objection to the original classification was that a large number of phenomena appeared twice. It is very unsatisfactory to find that in five years Nernst has made no real progress. In fact it would hardly be too much to say that he has gone backward. In the first edition he put the phase rule in the wrong part of the book ; but, at that time, there was the excuse of ignorance for such a mistake. The mistake has been repeated in the second edition, and an attack is made on Roozeboom for stating that the phase rule offers the best basis for a classification. To this Nernst makes the extraordinary reply that the phase rule says nothing about polyvariant systems and that the mass law and the theorem of van 't Hoff are much more important than the phase rule. This confirms the general impression already obtained that the fundamental principles of a good classification do not appeal to Nernst. The beauty of the phase rule is that, though qualitative, it is absolute and applies to every case of equilibrium, including the polyvariant systems. It is therefore the framework on which everything must rest. Whether the primary division is according to components and the secondary one according to variance, or vice-versa, depends on the relations which are to be emphasized ; but one or the other should be adopted if really satisfactory results are to be obtained. Having the framework, it is possible to fill in. While the phase rule applies to all systems, its results are exceedingly general. The direction of a change can be learned qualitatively from the theorem of Le Chatelier and quantitatively from the mass law and the theorem of van 't Hoff. The quantitative relations should always be considered with reference to the phase rule classification. Nernst has not done this and has evidently fallen into the error of supposing that the phase rule and the mass law are in some mysterious way mutually exclusive, whereas they are really supplementary. His mistake really rests on a false analogy. He compares the rôle of the phase rule in physical chemistry to that of the law of the conservation of mass in general chemistry. The two have the common characteristic of being rigidly true ; but, in some ways, it would have been more accurate to have compared the position of the phase rule in physical chemistry with that of the periodic system in inorganic chemistry.

The second edition contains only about one hundred pages more than the first edition, so that it is evident that the author has devoted himself energetically to the task of compressing the new material that has accumulated in such quantities in the past five years. Unfortunately it appears that there has been quite as much omission as compression. Giving references to all the more important papers on any subject does not necessarily involve a discussion of the articles and is of great assistance to those who rely on the text-books to find out what has or has not been accomplished. This volume of Nernst's will not be very serviceable to such people. Taking merely the one subject of reaction velocity as typical, there are no references to Long's work on the catalytic action of salts; to de Hemptinne's paper on the catalysis of esters; to the decomposition of diazo compounds studied by Hausser and Müller; to the change of metaphosphoric into orthophosphoric acid (Sabatier); to the change of synaldoximes into antialdoximes (Ley); to Wagner's work on the amidosulfonic acids; to Trevor and Kortright's method of following the reaction velocity by means of the boiling-point; to the work of Kastle, Murrill and Frazer; to the papers of Petersen, Tafel, Burchard, Gennari, Hantzsch and Miolati, Moro, Schwicker, and Storch, not to mention others. The work of Carrara on the effect of the solvent has been overlooked.

Most of the mistakes in the first edition are to be found in the second. The effect of pressure on the electromotive force of the Clark cell is ignored; the application of the mass law to the case of hydrates in solution is reprinted without change; there is nothing to show that the distribution law cannot apply rigidly when the third component is a liquid. In view of the extra space accorded to electrochemistry, it is a little surprising to find no discussion of the calomel electrode. A careful study of the book will make it plain that the revision has been a perfunctory one, that it was a task to be got through with, and that consequently the volume does not represent adequately the present state of the science. *Wilder D. Bancroft*

Physical Chemistry for Beginners. *By Ch. van Deventer. Translated by R. A. Lehfeldt. 13 × 19 cm; pp xvi and 146. London: Edward Arnold, 1898. Price: cloth 2s. 6d.*

Physical Chemistry for Beginners. *By Ch. van Deventer. Translated by Bertram B. Boltwood. 13 × 19 cm; pp. x and 154. New York: John Wiley and Sons, 1899. Price: cloth $1.50.*

The German edition has been reviewed in this Journal (1, 671). The work of both translators is good. It seems unfortunate that two translations should have appeared simultaneously in this way. It is a striking instance of how desirable it would be, if only a sort of scientific clearing house could be established; a general bureau where record would be kept of all work going on in all laboratories. Before undertaking a piece of work an investigator could then be certain the field was clear and the saving of time, now lost by useless duplication, would surely be great. *S. L. Bigelow*

NOTES ON THE ENERGY THEORY

BY J. E. TREVOR

I. The Energy Equation

The energy theory is a formulation of the relations that obtain between the measurable elements of phenomena. It presupposes, therefore, the fundamental postulate of physical science, the law of causality, that all physical changes are related directly or indirectly to one another.

The possibility of giving a quantitative formulation to this law of causality arises from the recognition that mechanical *work* can be produced only at the expense of some outstanding physical change, and that expenditure of work is always attended by a corresponding change. All physical phenomena being interrelated, all therefore present a mechanical side; so all possible physical changes can be brought into relation with the production or expenditure of mechanical work.[1] Changes, further, which result from expenditure of the same amount of work must be *equivalent* in a work sense, else combinations of such changes could be made to yield uncompensated work (a perpetual motion). We can, therefore, define the **work-equivalent** of any definite physical change as a quantity that is measured by the work which must be expended to produce the change. Thus, the work-equivalent E_{12} of the transport of the weight w through the height $h_2 - h_1$ against gravity is

$$E_{12} = w(h_2 - h_1).$$

The work-equivalent E_{12} of the change of the rectilinear velocity $v = ds/dt$ of a body from v_1 to v_2, is, from

$$f = m\frac{d^2s}{dt^2},$$

$$f\frac{ds}{dt}\,dt = m\frac{d^2s}{dt^2}\frac{ds}{dt}\,dt$$

$$E_{12} = \frac{m}{2}(v_2^2 - v_1^2).$$

[1] Compare Mach's writings on this subject.

The work-equivalent of the change of temperature of a body may be expressed in units of the mass of water whose temperature would be raised through a fixed standard difference of temperature by means of the action employed. And so on, indefinitely.

With the aid of these conceptions of work and of the work-equivalents of physical changes, we can formulate the law of causality in the statement that in any physical change the algebraic sum of all the developments of work and work-equivalents vanishes. Or, stated otherwise: The algebraic sum of all the work and work-equivalents added to any given system of bodies during any change of the system, is the change of a definite function of the independent variables whose values determine the state of the system. For, if this were not so, it would be possible to gain uncompensated work from cyclical operations following different paths between two end states of the system. The function in question is called the **energy E** of the system. It will be noted that this quantitative formulation of the fundamental scientific postulate is an *integral* principle.

It must not be overlooked that the work added in a change of state of a system of bodies is not a function of the state-variables x_1, x_2, ... of the system; and, also, that the work-equivalents thereby added are not such functions. The same change of state can always be effected by adding work W and work-equivalents E in different ratios; that is, the variations of these quantities are functions of the *changes* of the state-variables. This state of affairs is most suitably indicated by writing

$$d'\mathrm{W} = \mathrm{Y}_1 dx_1 + \mathrm{Y}_2 dx_2 + \cdots$$
$$d'\mathrm{E} = \mathrm{X}_1 dx_1 + \mathrm{X}_2 dx_2 + \cdots;$$

where the Y's and the X's are functions of the state-variables, and the notation[1] d'W and d'E indicates that the quantities W and E are not such functions. Adopting, further, the notation[1]

$$\mathrm{W}_{12} = \int_1^2 d'\mathrm{W}, \qquad \mathrm{E}_{12} = \int_1^2 d'\mathrm{E},$$

[1] W. Voigt. Kompendium der theoretischen Physik. Vol. I. p. 21 (1895).

where the indices refer to different states of the changing system, the energy law

$$\mathbf{E}_2 - \mathbf{E}_1 = \mathrm{W}'_{12} + \mathrm{W}''_{12} + \cdots + \mathrm{E}'_{12} + \mathrm{E}''_{12} + \cdots$$

may be cast into the differential form

$$d\mathbf{E} = \Sigma d'\mathrm{W} + \Sigma d'\mathrm{E}, \qquad (1)$$

where the summations are extended over all the different forms in which work and work-equivalents are added to the system. From this recapitulation of the fundamental ideas of the energy theory we see clearly that *it is essential to distinguish, in the energy equation, between work terms and work-equivalent terms.*

From the definition of work, we know that each of the work terms of equation (1) has the form $\mathfrak{P}d\mathfrak{p}$, where $\mathfrak{P}$ is a force (proportional to mass and acceleration), and $d\mathfrak{p}$ is a change of space. The quantity $\mathfrak{P}$ may, for example, be a force applied at a point, or a force applied at a line (a tension), or a force applied upon a surface (a pressure); the corresponding $d\mathfrak{p}$ being then, successively, either the differential of a distance, of a surface, or of a volume. Now, in order to utilize equation (1) to find relations involving the parameters that govern the transfers of work equivalents, it becomes necessary similarly to express the work-equivalent terms $d'\mathrm{E}$ with the aid of these parameters and their changes. To do this is the object of 'the potential theory'.

II. Potentials

1. Potentials uniquely determinate. — We may imagine that any definite physical change can be effected through the expenditure of work. Work can, for example, be expended to change the relative positions of bodies in a field of gravity, to change the velocity of a moving body, to change the electrostatic attraction between electrified bodies, to change the temperature of a body. And, if such actions are executed reversibly, no surplus work will be wasted in other changes, and the work that has been added can be regained through reversal of the operations. The result, then, of each such operation is *to*

store work as the work-equivalents of the change that is effected.

Different stores of any same kind of work-equivalents may be regarded as having different physical **levels,** when work must be expended, positively or negatively, reversibly to transfer work-equivalents from the one store to the other. Stores having the same height, or velocity, or temperature, etc., have then the same levels.

When an expenditure of work gives rise to no change, in the system of bodies acted upon, other than the change of level that it is desired to produce, the result of the operation is to start with the initial store E_1 of work-equivalents of the system at the initial level, to add reversibly the work w, and to close with the total store of work-equivalents $E_2 = E_1 + w$ at the final level. This operation is represented schematically in the accompanying Fig. 1. When, on the other hand, the change of level cannot be effected in a single direct operation, without simultaneously producing further change in the state of the system of bodies acted upon, the same result as before can be achieved by passing the system through a reversible cycle of operations made up of two paths at the two different constant levels, their ends being joined by two 'adiabatic' paths, — i. e. paths in which no work-equivalents are added to the working system, paths subject to the condition $d'E = 0$. This can always be done when, as supposed, work can be expended to effect the change that is in question. The working system being hereby returned to its initial state at the close of the operation, no permanent change is effected other than assumption of work-equivalents E_1 at the initial level, addition of work w, and deposition of work-equivalents $E_2 = E_1 + w$ at a store at the second level. We thus attain the same net result as before. The whole operation may be termed a *Carnot cycle.*

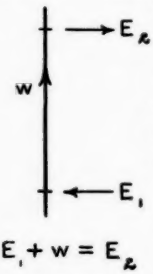

Fig. 1

In order to obtain a quantitative measure of the differences of level of different stores of the work-equivalents of any given kind of change, these differences are measured by the number of

equal increments of work required to traverse them *in a certain definite series* of reversible operations, these operations being Carnot cycles when necessary. This series shall be so constructed that the work-equivalents assumed by the working system at each level shall be equal to those deposited there in the preceding operation. The differences of level so measured shall be termed the differences of **potential** of the stores of work-equivalents.

The difference of potential between any two fixed levels is a constant quantity, — it is not dependent upon the path pursued between the two. For: Let the diagrams *a* and *b* of the accompanying Fig. 2 represent any two reversible paths, Carnot

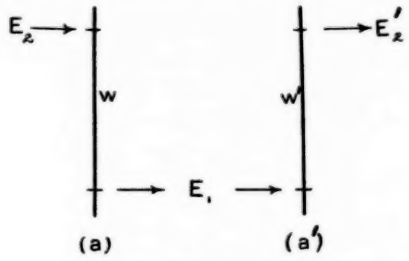

Fig. 2

cycles if necessary, between two stores at the different levels 1 and 2; and let it be supposed that the work-equivalents E_2 are taken up at 2. Reversible transport to 1, along the path *a*, yields the work w; and the work-equivalents E_1 are deposited at 1. Here, of course, $E_2 = w + E_1$. Let, now, E_1 be taken up for transport along the path a': work w' will be required, to deposit the sum $E_1 + w' = E'_2$ at the initial level 2. Nothing else occurs. Suppose now the quantities w and w', which measure the difference of potential of the two levels, to be not equal: say

$$w > w'.$$

Then

$$E_2 > E'_2,$$

and the two operations taken together would yield the gain of work

$$w - w'$$

at the expense of the work-equivalents $E_2 - E'_2$ taken from the store at the constant level 2. This result, however, is impossible, since work-equivalents at a constant level cannot be converted reversibly into work, — outstanding changes being excluded. Hence

$$w = w';$$

that is to say, the difference of potential of the two stores of work-equivalents is a constant quantity. So we see that the potential of a store of work-equivalents is determinate, except as to an additive constant, when the state of the system carrying the store is fixed; or, in other words, that the potential is a definite function of at least one of the state-variables of the system.[1]

It might be objected, to be sure, that in the isothermal expansion of a gas, for example, work can be obtained from a store of thermal work-equivalents at constant thermal level (constant temperature). This operation, however, differs wholly from those considered above, in that it involves an outstanding change of state of the gas at the close of the expansion.

2. Quantity-coordinates. — Let us consider the definite series of operations that serves to define the scale of potentials of a series of stores of the work-equivalents of any given kind of change. We will suppose these operations to be reversible Carnot cycles, — which indeed they *may* be in all cases. Representing the potentials along a vertical scale, we may represent the series by some such schematic arrangement as that of Fig. 3. In the first cycle the work-equivalents $E_0 = 0$ will be taken up at zero potential; wherefore the work-equivalents taken up in each

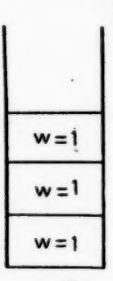

Fig. 3

[1] The potential being a function of the level, it is a function of the state-variables that determine the level. Thus the gravitation potential, and the thermal potential, are each functions of but one variable; while Gibbs's chemical potential of a component, in an n-component phase, is a function of the $(n-1)+2$ variables that are necessary to fix the chemical level.

successive cycle will equal the total work stored, up to that point, in the series of operations. That is, at the general value V of the potential, it will be V.

In a similar series of cycles, but in which the m-fold quantity of work is added in the first cycle, the work-equivalents added in the second cycle must be m-fold the previous value, namely $E_1 = m$. Continuing to add the m-fold work in each cycle, the work-equivalents added in the third operation will be $E_2 = 2m$; and so on. At the general potential V, accordingly, the work-equivalents added will be Vm. This state of affairs is represented in Fig. 4.

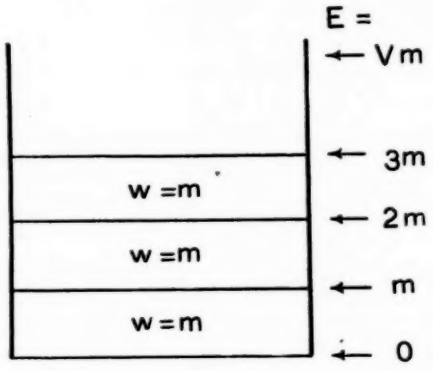

Fig. 4

So we see that the ratio of either of the quantities E of work-equivalents, added (positively or negatively) to a working system in any reversible Carnot cycle, to the potential V at which it is added, is necessarily

$$\frac{E}{V} = m,$$

— is proportional to the work taken up in any one of the cycles of the corresponding series, one cycle being introduced for each unit of difference of potential.

For the two additions of work-equivalents to the cycle, we have, therefore,

$$\left.\begin{aligned} \frac{E_2}{V_2} &= m \\ \frac{E_1}{V_1} &= m, \end{aligned}\right\}$$

from which we can conclude that, keeping the two potentials constant, an m-fold change of the E_1 will determine an m-fold change of the E_2 also. But these changes will furnish the two isopotential paths of a new cycle, since a cycle with m-fold E_1 may be shown to be identical in result with m cycles, each taking up the original E_1. Wherefore, in any reversible Carnot cycle *the change of the quantity* m *is the same along each isopotential path.* We may say indeed, and very suitably too, that the cycle serves *to transport* the m from the one potential to the other.

It follows herefrom that any finite reversible change of state, say from the state a to the state b in the accompanying representation of Fig. 5, which is combined from the preceding Figs.

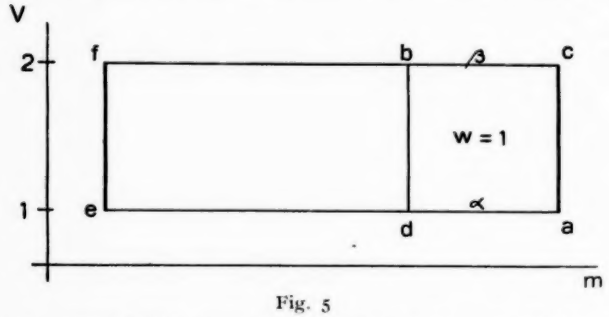

Fig. 5

3 and 4, completely determines the change $m_b - m_a$ of the quantity m. For, the change of m is the same along the path β that it is along the path α, and m has equal values at a and at c. The quantity E_{ab} of work-equivalents taken up in the reversible change from a to b is, however, for example, not determined by the change of state, — it depends upon the path pursued between

the two states. Along the path *a d b*, to illustrate, it would be

$$E'_{ab} = V_1 ; \qquad (a)$$

while along the path *a e f b* it would be

$$E''_{ab} = V_1 m - V_2 (m - 1),$$

or, since $V_2 = V_1 + 1$,

$$\begin{aligned} E''_{ab} &= V_1 m - (V_1 + 1)(m - 1) \\ &= V_1 - m + 1, \end{aligned} \qquad (b)$$

which is altogether different from (*a*).

Now, any reversible addition E of work-equivalents to a working system, even though it be made at continuously varying potentials, may be regarded as a sum of infinitesimal elements $d'E$, each added at a constant potential. The relation

$$\frac{E}{V} = m$$

for any reversible isopotential path may, therefore, for any reversible change whatever, be written

$$\frac{d'E}{V} = dm. \qquad (2)$$

And since the quantity m is a function of the state-variables of the working system, as has just been shown, it appears that the potential V is an integrating divisor of the differential addition

$$d'E = X_1 dx_1 + X_2 dx_2 + \cdots$$

of work-equivalents. Our general relation (2) is, thus,

$$\frac{X_1 dx_1 + X_2 dx_2 + \cdots}{V} = dm(x_1, x_2, \cdots),$$

where V is a differentiable function of one or more of the state-variables $x_1, x_2, \cdots$. The function

$$m(x_1, x_2, \cdots)$$

may very suitably be termed the **quantity-coordinate** of the work-equivalents that are added.

Clearing equation (2) of fractions, we have

$$d'E = V dm ; \qquad (3)$$

that is to say, we have expressed the work-equivalents differential in terms of the two differentiable functions V and m of the state-variables of the working system whose changes of state are under consideration. This result transforms equation (1)

$$\begin{aligned} d\mathrm{E} &= \Sigma d'\mathrm{W} + \Sigma d'\mathrm{E} \\ &= \Sigma \mathfrak{P} d\mathfrak{p} + \Sigma d'\mathrm{E} \end{aligned}$$

into

$$d\mathrm{E} = \Sigma \mathfrak{P} d\mathfrak{p} + \Sigma \mathrm{V} dm, \tag{4}$$

or, more fully written out,

$$\begin{aligned} d\mathrm{E} = {} & \mathfrak{P}' d\mathfrak{p}' + \mathfrak{P}'' d\mathfrak{p}'' + \cdots \\ & + \mathrm{V}' dm' + \mathrm{V}'' dm'' + \cdots, \end{aligned}$$

where the accents relate to the different forms in which work is added, and in which work-equivalents are added, during the reversible changes of state that the system undergoes.

This equation (4) represents the net result of the energy theory so far: namely, that all reversible changes of the energy of any system of bodies are the sums of work-terms and of work-equivalent terms; and that the work-terms are the products of forces into changes of space, while the work-equivalent terms are products of potentials into changes of quantity-coordinates. It is particularly important to bear in mind that one should distinguish not only between the work-terms and the work-equivalent terms, but also between the *forces* $\mathfrak{P}$ and the *potentials* V. The forces are not potentials, and the potentials are not forces. The former are true forces, proportional to mass and acceleration; while the latter are the amounts of work requisite to transport the corresponding unit quantity-coordinate from one physical level to another. In the term $-pdv$ for reversible compression work, for example, the force p is *not* the amount of work requisite to transport unit volume of the compressed body from one pressure to another. There has been much confusion concerning this matter, in the physicochemical literature of recent years.

[*To be continued.*]

MINIMUM BOILING-POINTS AND VAPOR COMPOSITIONS

BY J. H. PETTIT

I. Minimum Boiling-points

In the general discussion of systems made up of two volatile components, Bancroft[1] makes the following statement: "If two consolute liquids have the same vapor-pressure at a given temperature, some mixture of the two must have either a maximum or a minimum vapor-pressure at that temperature unless all concentrations have the same value. If at other temperatures the isothermal curve has neither a maximum nor minimum, it is possible to pass by change of temperature from a system behaving in one way to a system behaving in another. This would prevent any deductions from the form of the pressure curve at one temperature to that at another. *The alternative is that all consolute liquids with intersecting vapor-pressure curves form solutions with a maximum or minimum value at some concentration.*"

At the time this theorem was announced (1897), it could not be tested owing to the lack of experimental results. Since then, however, work has been done in this laboratory by Thayer[2] whose results showed that the theory held in three out of the four cases examined. The object of the present investigation was to test the theory still further by making use of different solutions.

The substances chosen for the work were solutions of acetone, chloroform and ether in methyl alcohol, as it was thought that the vapor-pressure curves of the first three each cut the methyl alcohol pressure curve. It is a matter of regret that the materials

[1] Phase Rule, 119.

[2] Jour. Phys. Chem. **2**, 382 (1898); **3**, 36 (1899).

chosen were the same as those used by Haywood,[1] but the work was completed before it was known that he was working in this field.

The methyl alcohol used was a so-called acetone-free material, obtained from Bender and Hobein. As considerable acetone was found in it, it was treated with caustic potash and iodine, the iodoform filtered off, and the filtrate allowed to stand over calcium oxide. It was afterward carefully fractioned, the first and last fractions discarded, while the part distilling over between 64.0° and 64.2° at a pressure of 739 mm was retained. This gave a boiling-point of 65.52° corrected to 760 mm. The data in the literature concerning the boiling-point of methyl alcohol seems to be somewhat confused — for instance, Ladenburg[2] gives two boiling-points — one 64.8°[3] at 763 mm. pressure, the other 65.4°[4] at 756.6 mm. Schmidt[5] in his work on the vapor-tension of homologous compounds made use of methyl alcohols of two different boiling-points — 66.6° and 64.9° at the same pressure of 777.5 mm. A comparison of the results obtained by Schmidt, Regnault,[6] Richardson,[7] Landolt,[8] Dittmar and Fawsitt[9] on the vapor-pressure of methyl alcohol shows that their results do not agree. The uncertainty as to its real boiling-point is therefore very apparent, and shows the difficulty in obtaining pure methyl alcohol. The large amounts needed in this work precluded the use of the oxalate method of purification. Tests made on the alcohol used failed to detect the presence of acetone or methyl acetate so that it is believed that the material was quite pure — sufficiently so at least to ensure the validity of all conclusions which will be drawn from the results given.

[1] Jour. Phys. Chem. **3,** 317 (1899).
[2] Handwörterbuch, **7,** 219.
[3] Schiff. Liebig's Annalen, **220,** 100 (1883).
[4] Konowalow. Wied. Ann. **14,** 40 (1881).
[5] Zeit. Phys. Chem. **8,** 630 (1891).
[6] Mém. de l' Académie, **26,** (1862).
[7] Inaug. Diss., Freiburg, 1886.
[8] Liebig's Annalen, Suppl. **6,** 129 (1868).
[9] Trans. Roy. Soc. Edinb. **23,** II. 509 (1886-87).

The main impurity of the acetone used was found to be water. This was removed by distillation with a Hempel column, the part coming over between 55.5° and 56.1° at a pressure of 747 mm, being retained. The boiling-point of this fraction when corrected, corresponds to the generally accepted one of 56.52° at 760 mm.

The method used for the purification of the chloroform was that given by Linebarger.[1] The material was washed twelve times with water, and then shaken with a concentrated solution of calcium chlorid. After this treatment, the chloroform was fractioned through a Hempel column. The part kept was that distilling over between 60.0° and 60.3° at a pressure of 741 mm. The corrected boiling-point of this fraction was found to be 61.97°, which is much higher than the one ordinarily given, 61.2°, although it agrees with the boiling-point as determined by Thayer.[2] The impurity causing this high boiling-point we have not discovered.

Since ether which has dissolved in it slight amounts of water has a boiling-point differing very little from that of pure ether, care was taken to remove the water by repeated distillation over calcium chlorid. The boiling-point of the ether thus obtained was 34.97° at 760 mm.

The apparatus used in the determination of the boiling-points was that of Orndorff and Cameron.[3] The Beckmann apparatus in its ordinary form is not suited to the determination of boiling-points where both components are volatile, although in the present instance it could have been modified for the work by lessening the vapor space above the solution.

The thermometers used were divided into tenths of degrees so that readings could be made to $\pm 0.01°$. The thermometers were carefully compared with a Reichsanstalt, and all the readings given are corrected for the error due to the part exposed in the air. The readings given should therefore be correct to the

[1] Jour. Am. Chem. Soc. **17**, 648 (1895).
[2] Jour. Phys. Chem. **3**, 37 (1899).
[3] Am. Chem. Jour. **17**, 517 (1895).

first decimal place. The pressures given are corrected but not reduced.

In the first table are given the results obtained in determining the boiling-point curve for all possible mixtures of methyl alcohol and chloroform. In the first column is given the percentage of alcohol in the mixture expressed in grams, in the second column the percentage of acetone, in the third column the barometric pressures under which the boiling-points recorded in the fourth column were made. As these pressures differ so little from their mean value of 746.2 mm, the correction due to the reduction to the mean pressure will be very small. The boiling-points thus corrected (on the basis of a change in the boiling-point of 0.04° per mm of pressure) are given in the fifth column.

TABLE I

Alcohol	Chloroform	Bar	B Pt	B Pt corr	Alcohol	Chloroform	Bar	B Pt	B Pt corr
100.0	0.0	747.0	64.85°	64.82°	40.2	59.8	745.7	56.10°	56.12°
89.6	10.4	746.7	63.56	63.54	31.0	69.0	745.5	55.00	55.03
80.8	19.2	746.7	61.90	61.88	22.5	77.5	745.5	54.30	54.33
73.6	26.4	746.7	61.30	61.28	15.4	84.6	745.5	53.80	53.83
67.4	32.6	746.7	60.25	60.23	11.9	88.1	745.5	53.60	53.63
58.1	41.9	746.7	58.80	58.78	8.2	91.8	745.5	53.60	53.63
49.4	50.6	746.7	57.30	57.28	0.42	99.58	745.5	54.40	54.43
48.0	52.0	746.7	57.30	57.28	0.0	100.0	746.0	61.45	61.46

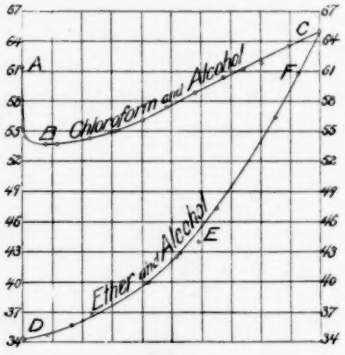

Fig. 1

The results presented in this table are represented graphically by the curves ABC, Fig. 1. The great pitch of the curve when a very small amount of alcohol is added to the chloroform shows that a very slight amount of this substance as impurity in chloroform would show itself very readily. The minimum boiling-point occurs at about 53.5° at a pressure of 746.2°, where the composition

is approximately 90 percent chloroform and 10 percent methyl alcohol.

The table for methyl alcohol and ether (Table II) is arranged in a manner similar to the first. In this case also the pressures vary but little from the mean value of 738.7, but nevertheless the correction has been applied here also.

TABLE II

Alcohol	Ether	Bar	B Pt	B Pt corr	Alcohol	Ether	Bar	B Pt	B Pt corr
100.0	0.0	737.8	64.90°	64.94°	51.1	48.9	738.6	42.50°	42.50°
92.2	7.8	738.1	60.60	60.62	42.3	57.7	738.8	39 90	39.90
85.0	15.0	738.3	56.30	56.31	22.9	77.1	738 8	36.65	36.65
65.3	34.7	739.3	47.20	47.18	16.4	83.6	738.8	35.65	35.65
59 4	40.6	738.8	44.00	44.00	8.8	91.2	738 8	34.70	34.70
52.5	47.5	738.8	42.92	42.92	0.0	100.0	739.1	34.20	34.21

The curve DEF in Fig. 1 expresses the results given in the preceding table. It possesses neither maximum nor minimum.

The results obtained for acetone and methyl alcohol are presented in Table III which is arranged in the usual manner. In this case also, it is possible to correct to the mean barometric pressure, but as the table is to be used later in the determination of vapor compositions, it has been reduced to the standard pressure of 760 mm. The corrections have been taken from Landolt and Börnstein's Tabellen (p. 191) which gives the value of 0.037° as corresponding to 1 mm increase of pressure for alcohol between the pressures of 730 and 760 mm, while for acetone the same value is 0.039°. For all mixtures mean values have been assumed depending on the proportions of each present. Values obtained in this way may not be rigidly accurate, but in the absence of more reliable data may be assumed as very nearly correct.

TABLE III

Alcohol	Acetone	Bar	B Pt	B Pt corr	Alcohol	Acetone	Bar	B Pt	B Pt corr
100.0	0.0	720.6	64.30	65.52	45.0	55.0	729.7	56.50	57.65
89.1	10.9	726.4	62.20	63.44	31.0	69.0	729.4	55.50	56.68
80.5	19.5	726.9	60.75	61.98	23.1	76.9	728.9	55.10	56.29
58.6	41.4	727.7	57.75	58.96	18.6	81.4	728.9	54.90	56.09
53.7	46.3	727.7	57.30	58.52	13.2	86.8	728.9	54.80	55.99
51.9	48.1	729.7	57.20	58.34	6.6	93.4	728.9	54.90	56.09
49.0	51.0	727.7	56.80	58.02	0.0	100.0	728.4	55.40	56.62

The curve GHK which gives the representation of these results is shown in Fig. 2. A minimum boiling-point occurs at a temperature of 55.93° at a pressure of 760 mm, the composition of the solution being approximately 13.5 percent alcohol and 86.5 percent acetone.

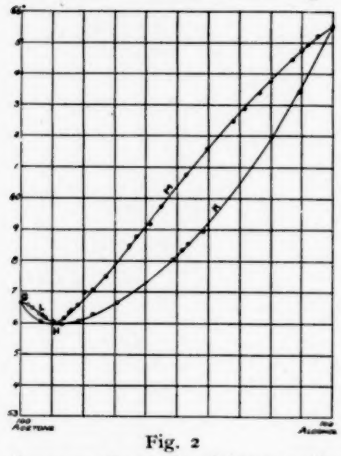

Fig. 2

In testing the conformity to the theory of the results which have so far been given in connection with boiling-point determinations, it will be well to refer to a paper which gives a very fair summary of vapor-pressure determinations up to the year 1894. In this paper the author[1] has gathered the most satisfactory measurements of vapor pressures of different compounds with the idea of finding what vapor-pressure curves intersect. The difficulty of access to this paper, the fact that it has been overlooked by at least one scientist, and its use for further reference, make excuse for its insertion completely unnecessary. The paper proceeds as follows:

"I shall limit myself to merely recalling the measurements of Sajotschewsky[2] whose curves do not intersect and proceed at once to those of Ramsay, Young and Thomas[3] which are more interesting from a double standpoint — the boiling-points of the liquids examined are much closer to each other, and the accuracy of the measurements is of a very high order.

"In the following table will be found non-associated liquids arranged in the order of rising boiling-points, if we regard these

[1] Guye. Arch. de Genève, (3) **31**, 164 (1894).

[2] Sajotschewsky. Beiblätter, **3**, 741 (1879).

[3] These measurements have been published in articles written by Ramsay and Young, Young, and Young and Thomas. Recapitulation of the results obtained may be found in the two articles: S. Young. Phil. Mag. [5] **34**, 512 (1892), and S. Young and Thomas. Jour. Chem. Soc. **63**, 1259 (1893).

boiling-points as taken under a pressure of 760 mm of mercury. As a matter of fact the determination of the molecular weight in the state of liquid has not been made for all the compounds, but according to all analogy it is almost certain that all the bodies mentioned in this table are not polymerized in the liquid state, at least not to an appreciable extent.

		P = 200 mm	P = 760 mm	P = 4000 mm	P = 25000 mm
1	Methyl formate	+0.5	31.8	81.0	175.0
2	Ethyl ether	1.6	34.5	91.6	189.1
3	Carbon bisulfid	10.1	46.2	107.5	202.5
4	Ethyl formate	20.8	54.3	112.4	210.8
5	Methyl acetate	23.5	57.3	114.3	210.7
6	Carbon tetrachlorid	38.7	76.8	114.3	258.3
7	Ethyl acetate	41.6	77.1	138.3	240.4
8	Methyl propionate	43.9	79.7	141.0	244.7
9	Benzene	42.4	80.3	146.0	258.8
10	Propyl formate	45.0	80.9	143.8	250.6
11	Fluor benzene	47.3	85.1	150.8	263.0
12	Methyl isobutyrate	55.0	92.3	157.3	265.6
13	Ethyl propionate	61.6	99.0	164.3	272.3
14	Propyl acetate	63.6	101.6	167.1	275.7
15	Methyl butyrate	64.3	102.7	168.7	278.3
16	Tin tetrachlorid	73.0	114.2	186.0	309.1
17	Chlorbenzene	80.0	131.9	206.9	....
18	Brombenzene	110.1	156.0	235.0	....
19	Iodbenzene	139.2	188.6	272.7	....

"By following these columns from top to bottom, it may be readily seen that the temperatures of ebullition under the pressures of 200, 4000 and 25000 mm of mercury, increase gradually in exactly the same manner as those given for the pressure of 760 mm, which determined the foregoing arrangement; the only exceptions are the fatty ethers whose boiling-points lie close to those of benzene and carbon tetrachlorid, for which the vapor-tension curves cut at a few tenths of a degree below the pressure of 760 mm. These exceptions are possibly attributable to the fact that some ethers begin to decompose when they are heated to high temperatures: this fact has been announced by

[1] Battelli. Atti. Accad. Sci. Torino, (2) 42.

Nadesjdine[1] and has been confirmed by Young and Thomas.[2] The general statement may therefore be made that non-associated liquids give vapor-tension curves which do not intersect.

"In addition to the preceding results, there are now to be given the boiling-points of bodies made up of polymerized molecules, under the extreme range of 200 and 25000 mm.

	$p = 200$	$p = 25000$
Water	66.5	239.9
Methyl alcohol	34.5	191.0
Ethyl alcohol	48.1	206.2
Propyl alcohol	67	237
Acetic acid	79.7	282.5

From these data, it follows that at the pressure of 200 mm the vapor-tension curve of water passes between those of methyl butyrate (64.3°) and tin tetrachlorid (73.0°); at the pressure of 25000 mm it passes between those of ethyl acetate (240.4°) and methyl acetate (210.7°); this curve should therefore cut the curves of all the intermediate bodies bearing the numbers 6 to 15. According to its boiling-point under the pressure of 200 mm, methyl alcohol should be placed between methyl acetate and carbon tetrachlorid; while under the pressure of 25000 mm the boiling-point of methyl alcohol lies between those of ethyl ether and carbon bisulfid; the vapor-tension curve of this alcohol cuts therefore those of the four intermediate bodies, methyl acetate, ethyl formate, carbon bisulfid and ethly ether.

"By analogous reasoning it might be really proved that the curve for ethyl alcohol cuts the curves of liquid Nos. 4, 5, 6, 7, 8, 9, 10, and 11; propyl alcohol the curves, Nos. 6, 7, 8, 9, 10, 11, 12, 13, 14, and 15; acetic acid only one curve, No. 16."

Up to the present there have been observed minimum boiling-points with the following pairs of completely miscible substances: methyl alcohol with carbon tetrachlorid,[3] acetone,[4] [5]

[1] Nadesjdine. Repertorium der Physik, Vol. 23.
[2] Young and Thomas. loc. cit.
[3] Thorpe. Jour. Chem. Soc. **35**, 547 (1879).
[4] Haywood. Jour. Phys. Chem. **3**, 317 (1899).
[5] This paper.

chloroform,[1] [2] methyl acetate[3] and methyl cyanide;[7] ethyl alcohol with carbon bisulfid,[4] chloroform,[5] benzene;[5] water and methyl cyanide[7]; allyl alcohol and water;[7] trimethyl carbinol and water;[7] acetone with carbon tetrachlorid;[1] ethyl acetate and carbon bisulfid;[4] water with butyric acid[6] or propyl alcohol.[6] Of these, the data collected by Guye show that the curve for methyl alcohol cuts the corresponding pressure curve for methyl acetate; that the curve for ethyl alcohol cuts the vapor-pressure curve for benzene, while water and propyl alcohol also have pressure curves which intersect.

Since only three of the sixteen cases enumerated are substantiated by the data here presented, it is necessary to submit the theory to a more careful test. There has accordingly been gathered from the most available source — mainly Landolt and Börnstein's Tabellen — the data from which conclusions may be drawn as to the intersection or non-intersection of each pair of curves. In the following table there are given in the first two columns the substances which are being examined; in the third column the approximate temperature, in the fourth the approximate pressure, at the point of intersection of the vapor-pressure curves; in the fifth column the name of the observer who examined the pressures of the liquid denoted in the first column, while the sixth holds the name of the observer who examined the substance named in the second column.

TABLE V

I	II	III	IV	V	VI
Pairs of substances		Temp of intersection	Pressure of intersection	Observer of first substance	Observer of second substance
Methyl alcohol	Carbon tetrachlorid	14.5°	70 mm	Young	Young
Methyl alcohol	Acetone	130	5600	Regnault	Regnault
Methyl alcohol	Chloroform	101.5	2550	Regnault	Regnault
Methyl alcohol	Methyl acetate	113.8	4000	Young	Young
Ethyl alcohol	Chloroform	148.5	7100	Regnault	Regnault
Ethyl alcohol	Benzol	71	570	Regnault	Regnault
Water	Propyl alcohol	41	58	Regnault	Schmidt

[1] Haywood. Jour. Phys. Chem. **3**, 317 (1899).
[2] This paper.
[3] Holly. Unpublished results.
[4] Brown. Jour. Chem. Soc. **39**, 529 (1881).
[5] Thayer. Jour. Phys. Chem. **3**, 39 (1899).
[6] Konowalow. Wied. Ann. **14**, 50, 219 (1881).
[7] Konowalow. Ber. chem. Ges. Berlin, **17**, 1536 (1884).

In the case of water and butyric acid, the data for the latter substance are lacking so that the theory cannot be tested for this case. With some of the remaining cases, it is necessary owing to insufficient data to resort to an examination of the critical temperatures and pressures to form an opinion as to the intersection of the curves. Thus in the case of ethyl alcohol and carbon bisulfid there may be found the following results. Boiling-point of ethyl alcohol at 760 mm is 78.4°, of carbon bisulfid 46.04°. At 25000 mm pressure ethyl alcohol boils at 206.2°, while carbon bisulfid boils at 202.5°. The critical temperature of ethyl alcohol is 234°, critical pressure 65 atmospheres, while Hannay and Hogarth determined the corresponding temperature for carbon bisulfid as 277° and the pressure at 78 atmospheres. Unless these curves change their directions in a discontinuous manner they must intersect not far below the critical temperature for ethyl alcohol.

Acetone and carbon tetrachlorid have boiling-points of 56.5° and 76° respectively, while the data for acetone (as determined by Sajotschewsky) give the critical temperature of acetone as 232.8°, and its critical pressure at 52.2 atmospheres. Young determined the critical temperature of carbon tetrachlorid as 283.15°, and its critical pressure as 44.9 atmospheres. The pressure curves do therefore undoubtedly intersect.

At ordinary pressures carbon bisulfid boils much lower than ethyl acetate, but its critical temperature is 277° at a pressure of 78 atmospheres (Hannay and Hogarth), while the corresponding data for ethyl acetate as determined by Sajotschewsky are 239.8° and 42.3 atmospheres. There can be little doubt therefore that these substances have intersecting pressure curves.

For the examination of the curves of methyl alcohol and methyl cyanid, ethyl alcohol and methyl cyanid, allyl alcohol and water, trimethyl carbinol and water, we have been unable to find data sufficient to allow of any conclusions being drawn. With respect to the case of ethyl alcohol and water, it must be remarked that the pressure curves do not intersect and it is extremely doubtful whether there is a minimum boiling-point in

the curve. This is one of the cases that requires very careful examination.

Of the cases examined recently where neither maximum nor minimum was found we may note that none of the following substances give intersecting pressure curves; methyl alcohol and water, acetone and water, or acetone and ether. With chloroform and carbon tetrachlorid, it is impossible from the conflicting data to judge accurately, but it is extremely probable that the pressure curves do not intersect. The curves for methyl alcohol and ether which Guye believed to possess a point of intersection do not cross.

This résumé covers all the cases where a minimum boiling-point which has been observed has come to our knowledge. The fact that all the cases which allow of close examination have shown that minimum boiling-points have been found when the pressure curves intersected, offers very strong confirmatory evidence of the reliability of the Bancroft theory as a useful working hypothesis, which will as the subsequent section will attempt to prove, be a very great help to every organic laboratory.

Other pairs of substances showing the same pressure at the same temperature have been noted by Kahlbaum[1] who however does not seem to have been aware of Guye's work. He states: "Up to the present such an intersection of two boiling curves was known only in the case of benzol and ethyl alcohol, and it is this fact which induced us to include alcohol in the field of our research; now our observations show that this phenomenon occurs very frequently also with closely related substances—of nine substances examined, five intersected." These pairs are benzonitrile with phenol or aniline, phenol with aniline, and benzyl alcohol and nitrobenzol. The inaccuracy of Kahlbaum's statements even if he refers only to substances at ordinary pressures may be seen very readily.

II. Vapor Composition

Determinations of the composition of the vapor phase which

[1] Kahlbaum. Zeit. phys. Chem. **26**, 605 (1898).

is in equilibrium with a definite solution are very few in number. So far as the writer is aware there has not been determined completely for one case the composition of the vapor phase in equilibrium with the different concentrations of a pair of substances which possess a minimum or maximum boiling-point.[1] Accordingly methyl alcohol and acetone have been chosen as the pair of substances for the investigation.

At first, recourse was had to the method of vapor analysis proposed by Carveth,[2] but owing to the slight difference in the boiling-points, it was impossible to convey heat to the liquid in the inner tube as rapidly as was required. Owing to the ease with which accurate determinations had previously been made by this apparatus, the result was quite unexpected, and while the Carveth apparatus was being subjected to further trials, the vapor curve was determined in the manner now to be described.

Into a liter balloon flask was fitted a cork containing one hole for the thermometer, and one for the tube leading to the condenser. The receiver held about 35 cc and had in it on the upper side a very small opening to equalize the pressure. The neck of the tube leading to the condenser was heated by an electric coil, and the thermometer was protected from radiation effects by asbestos wrappings. During the distillation, condensation on the walls of the flask or in the neck were carefully avoided. The distillate passing over between two definite temperatures (represented in Column I of Table II) was collected, and its boiling-point noted (Column IV). The barometric pressure having been observed (Column III), the mean boiling-point and the boiling-point of the distillate were corrected to the pressure of 760 mm in the manner described when giving the boiling-point curve for methyl alcohol and acetone. These corrected results are given in Columns II and V.

[1] Thorpe. Jour. Chem. Soc. **35**, 347 (1879), gives results with carbon tetrachlorid and methyl alcohol which can readily be calculated by representation, but he deals with only one side of the curve. The boiling-point curve, moreover, is not determined by direct experiment.

[2] Jour. Phys. Chem. **3**, 193, (1899).

TABLE IV

Distillate	Corr mean B Pt of solution	Bar	B Pt vapor	Corr B Pt vapor
55.70-55.88	56.67	734	55.52	56.40
55.50-55.70	56.48	734	55.42	56.30
55.30-55.50	56.28	734	55.26	56.14
55.30-55.30	56.22	734	55.22	56.10
55.20-55.30	56.17	734	55.20	56.08
55.00-55.20	56.02	734	55.06	55.98
55.00-55.20	56.16	735	54.98	55.93
55.20-55.28	56.30	735	55.00	55.95
55.28-55.40	56.40	735	55.04	55.95
55.50-55.70	56.54	735	55.14	56.08
56.00-56.14	56.94	737	55.28	56.15
56.14-56.20	57.04	737	55.40	56.27
56.50-56.68	57.46	737	55.58	56.45
57.50-57.80	58.52	737	56.04	56.91
57.80-58.00	58.77	737	56.20	57.07
58.20-58.40	59.17	737	56.60	57.47
58.70-59.10	59.77	737	56.84	57.71
59.56-60.30	60.77	737	57.60	58.47
60.30-61.30	61.67	737	58.42	59.29
61.40-61.80	62.47	737	59.30	60.17
61.80-62.24	62.89	737	59.76	60.63
62.24-62.68	63.33	737	60.44	61.31
62.68-63.12	63.77	737	60.96	61.83
63.40-63.78	64.46	737	62.06	62.93
63.78-64.00	64.76	737	62.56	63.43
64.00-64.20	64.97	737	62.90	63.77
64.20-64.50	65.22	737	63.62	64.49

These results are presented in the vapor composition curve (LHM) in Fig. 2. If one starts with a dilute solution (say five percent) of alcohol in acetone, it will be observed that the vapor phase in equilibrium with the solution contains a greater percentage of alcohol. Distillation will keep removing the alcohol along with much acetone of course, but the final substance left in the still will be pure acetone. Or, if one has as initial solution much alcohol and little acetone, the process of distillation will remove the acetone in greater percentage than it exists in the solution, and the final product in the still will be pure methyl alcohol. In either of these cases it is evident that the boiling-point of the solution in the still will rise as the distillation progresses.

At the point (H) however, vapor and solution have the same composition and therefore must, when distilled, show a constant boiling-point. A similar state of affairs would exist if a maximum boiling-point were present. The constancy of a boiling-point does not therefore prove conclusive evidence as to the purity of any substance unless proof has been adduced that any substance which has been present during the operation and which could give a maximum or minimum boiling-point has

been completely removed. This is important because it cannot be told whether a maximum or minimum will occur with fifty or with one-fifth percent of the second component. It is in cases like this that the Bancroft theory can give considerable assistance to the organic chemist.

If then one has for examination any two substances which give an abnormal boiling-point curve, it is apparent that no fractional distillation can separate the two substances completely. Ignorance of this fact has been the cause of frequent mistakes, though for illustration reference will be made merely to Otto[1] and to Monnet[2] who with their own superior distillation methods think they have separated acetone and methyl alcohol, getting pure acetone to pass over first. Reference to Fig. 2 shows the impossibility of such statements being accurate. The impossibility of completely separating methyl alcohol from chloroform, acetone and methyl acetate shows that the theories of distillation should be well understood by technical as well as purely scientific workers.

The constantly recurring mistake of believing that the proximity of boiling-points has anything to do with fractional distillation must be guarded against. It is true that many of the substances which have so far shown maximum or minimum boiling-points do have boiling-points lying not very far apart; but the ease of separation by distillation depends on the differences between the composition of the solution and the vapor.

In this paper there has been given: —

(1) The determination of three boiling-point curves, of which two showed a minimum.

(2) A complete test of the Bancroft theory making use of all the data known to us up to the present. The theory has been found supported by facts in every case which could be examined.

(3) The determination of the vapor composition curve for acetone and methyl alcohol.

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[1] Bull. Soc. Chim. Paris, (3) **11**, 197 (1893).

[2] Ibid. (3) **13**, 113 (1895).

(4) Conclusions as to the effectiveness of fractional distillation, and the usefulness of applying its theory to laboratory practice.

The work given in this paper has been performed under the direction of Dr. H. R. Carveth, Honorary Fellow in Chemistry.

Cornell University

DISSOCIATION PRESSURE BEFORE H. SAINTE-CLAIRE DEVILLE

BY P. DUHEM

I owe to the kindness of M. G. Brunel, Dean of the *Faculté des Sciences* of Bordeaux, my acquaintance with a little pamphlet[1] published in 1837 under the title: *De l'influence de la pression sur les actions chimiques*; this pamphlet is the thesis of Georges Aimé.

Born at Metz on the 27th of January, 1810, Georges Aimé entered the Ecole Normale in 1831, in the same class as Abria and Edouard Desains. The possessor of a precocious and fertile intelligence and gifted with an inquiring spirit which was attracted by a wide range of subjects, at the age of twenty-three he began a series of publications on organic and inorganic chemistry, geology, physics, and physiology. Between 1833 and 1837 he published a *Note sur le fluor*,[2] a *Note sur un procéde nouveau d'aimentation*,[3] a *Note sur la vision*,[4] a note *Sur les produits crystallises que présente la nature*,[5] a note entitled *De la masse du fluide électrique*,[6] researches *Sur l'action de l'alcool nitrique sur l'iode et sur le brôme, et de l'hydrate de methylène nitrique sur le même corps*,[7] and researches *Sur l'ether chlorocyanique et le chlorocyanate de méthylène*.[8]

[1] Thèse de Chimie, présentée et soutenue à la Faculté des Sciences de Paris le 9 novembre 1837 par M. (Georges) Aimé de Metz, (dép. de la Moselle), docteur ès Sciences. De l'influence de la pression sur les actions chimiques, in 4°, 16 pp. Paris. E J. Bailly, imprimeur. 1837.

[2] Ann. Chim. Phys. (2) **55,** 443 (1833).

[3] Ibid. **57,** 442 (1834).

[4] Ibid. **56,** 108 (1834).

[5] Bull. Soc. philomathique, **6,** 305 (1834–35).

[6] Ann Chim. Phys. (2) **62,** 419 (1836).

[7] Ibid. (2) **64,** 217 (1837).

[8] Ibid. (2) **64,** 220 (1837).

The 9th of November, 1837, Georges Aimé took, before the *Faculté des Sciences* of Paris, his examination for the degree of *docteur ès sciences physiques.* His first thesis was the work we have already mentioned, and to which we shall revert; his second thesis, reduced to what was then called a *programme* and which to-day is called *questions posées par la Faculté*, was entitled: *Actions exercées dans tous les corps par l'influence des courants électriques et des aimants.*

Soon after taking his degree, Georges Aimé was appointed professor of physics at the College of Algiers; from which time he devoted himself almost exclusively to researches on meteorology and on the physics of the earth. In 1839 he submitted to the Academy of Sciences the principal results of a *Mémoire sur le mouvement des vagues.*[1] In the meantime, the Minister of War had sent a scientific commission to Algeria, and the Royal Society of London had asked the Academy of Sciences of Paris that the commission should make a special study of the elements of terrestrial magnetism in that colony. At the meeting of November 25th, 1839, Arago declared[2] that the surest way to gratify the wish of the Royal Society of London was to add Aimé to the African scientific commission. "The request of the Academy has been twice transmitted to the Minister of War; no answer having yet been received, M. Arago suggests that he be again petitioned."

On the 2nd of December, 1839, "the Minister of War announces[3] that, in accordance with the wish expressed by the Academy that M. Aimé, Professor of Physics at the College of Algiers, be added to the Algerian scientific commission, he has included that physicist in a list of adjunct members, appointed to give aid in various ways, and whose services may deserve reward or remuneration to be granted by individual decisions."

On the 6th of January, 1840,[4] "the commission entrusted

[1] Comptes rendus, **9**, 409 (1839).
[2] Ibid. **9**, 703 (1839).
[3] Comptes rendus, **9**, 735 (1839).
[4] Ibid. **10**, 11 (1840).

with the care of providing the necessary instruments for the magnetic observations to be carried on in Algeria in accordance with the wish expressed by the Royal Society of London, proposes to ask of the Minister of War a leave of absence of several weeks for M. Aimé in order that, during his stay in Paris, he may compare the new instruments to be entrusted to his care with those of the Observatory." This appointment but added a new stimulus to the scientific zeal of Georges Aimé ; for he published numerous memoirs on meteorology and on the physics of the earth, with an occasional note on pure physics or chemistry.

In 1840, he published a *Mémoire sur les variations du niveau de la mer dans le port d' Alger*;[1] in 1841 a *Note sur les gaz dégagés par les plantes marines*[2] and a paper in German entitled : *Mittlere Temperatur in Algier*;[3] in 1842, *Recherches expérimentales sur le mouvement des vagues.*[4] At the meeting of January 9th, 1843, " M. Arago submits to the Academy[5] numerous observations on meteorology and on the physics of the earth that M. Aimé has made during his stay in Algeria." In the same year 1843, Georges Aimé published a *Mémoire sur un moyen nouveau de sonder à la mer*,[6] a *Mémoire sur la compression des liquides*,[7] and he began the publication of a *Mémoire sur le Magnétisme terrestre*;[8] in 1844 appeared a paper on the *Variations du niveau de la Méditerranée*;[9] in 1845, a *Mémoire sur les courants de la Méditerranée*,[10] and a *Mémoire sur les températures de la Méditerranée* ;[11] and, in 1846, an *Instruction sur l' emploi de l' anémometre par réflexion.*[12] But on the 9th of

[1] Ann. Chim. Phys. (2) **73,** 416 (1840).
[2] Ibid. (3) **2,** 535 (1841).
[3] Pogg. Ann. **54,** 448 (1841).
[4] Ann. Chim. Phys. (3) **5,** 417 (1842).
[5] Comptes rendus, **16,** 93 (1843).
[6] Ann. Chim. Phys. (3) **7,** 497 (1843).
[7] Comptes rendus, **16,** 1165 ; Ann. Chim. Phys. (3) **8,** 257 (1843).
[8] Comptes rendus, **17,** 1031 (1843) ; Ann. Chim. Phys. (3) **10,** 105 (1844); **17,** 199 (1846).
[9] Comptes rendus, **18,** 219 ; Ann. Chim. Phys. (3) **12,** 271 (1844).
[10] Ann. Chim. Phys. (3) **13,** 460 (1845).
[11] Ibid. (3) **15,** 5 (1845)
[12] Ibid. (3) **17,** 498 (1846).

September, 1846, death stopped Georges Aimé in the midst of his scientific activity; he was not thirty-seven years old.

Among the writings of Georges Aimé there is one which would have secured his fame if the ideas which it contains had been understood when they were published; we refer to his researches on the influence of pressure upon chemical reactions. The thesis of Georges Aimé indeed shows plainly that he had arrived at the notion of dissociation pressure thirty years before Debray, by his experiments, established its existence.

Properly to appreciate the meaning and the bearing of the new views of Georges Aimé, it is necessary to define the part assigned by chemists to pressure, and, for that purpose, to go back to the physico-chemical theories which were current at the end of the last and at the beginning of the present century, to the theories which formed the basis of the work of Lavoisier and Laplace.

According to these physicists, every body contains ponderable matter and caloric; the molecules of ponderable matter exert upon one another actions of affinity, which are attractive and which would bring the molecules into contact if they were not prevented by the actions of the caloric; these, on the contrary, tend to separate the molecules indefinitely.

The various states of equilibrium which natural bodies attain cannot be explained if the mutual affinity of the molecules and the actions of the caloric are alone taken into account. To these two kinds of forces, both of which are internal, it is necessary to add an external force: the pressure exerted by the atmosphere or by the surrounding bodies.

Moreover, here, as in every problem of mechanics, while the magnitude of this pressure plays an important part in the determination of the resulting phenomena, the origin of the pressure is of no importance. Suppose we ask, for example, if a given liquid at a given temperature will change or not into vapor? To answer this question we must know the magnitude of the pressure borne by the liquid, but it is a matter of

indifference whether the pressure be exerted by the vapor itself, by the atmosphere, or by any other body.

We find these ideas very definitely expressed in a passage of the *Traité élémentaire de Chimie*[1] of Lavoisier:

"We have seen that the same body takes the solid, liquid, or gaseous form according to the quantity of caloric which it contains, or more exactly, according as the repulsive force of the caloric is equal to, greater than, or less than the attraction of the molecules.

"However, if there were only these two forces, a body could exist in the liquid form at but a single temperature, and it would change suddenly from the solid to the gaseous state. Thus, for example, water, at the moment when it ceases to exist as ice, would begin to boil; it would take the gaseous form and its molecules would separate indefinitely. That this is not the case is due to a third force, the pressure of the atmosphere, which opposes this separation; and accordingly water remains in the fluid state from zero to 80 degrees of the French thermometer. The quantity of caloric which it absorbs in that interval is insufficient to overcome the action due to the pressure of the atmosphere.

"We thus see that without the pressure of the atmosphere we should not have any permanent liquid; we could observe bodies in the liquid state only at the moment when they melt, and the slightest addition of heat would then separate and disperse their parts."

These ideas, developed by Lavoisier with reference to the transformation of a liquid into vapor, were applied by Hutton[2] to chemical decomposition. Carbonate of calcium is decomposed by the heat of a lime-kiln into calcium oxide and carbonic acid; how then does it happen that we find marble and crystals of calc-spar in igneous rocks, whose temperature, at certain geological epochs, must greatly have exceeded the temperature of a lime-

[1] Lavoisier. Traité élémentaire de Chimie, Première Partie, Chapitre I.

[2] James Hutton. On the philosophy of light, heat and fire. Trans. Roy. Soc. Edinb. 4 (Hist.), 7 (1798).

kiln? According to Hutton, it is because calcium carbonate heated in a lime-kiln bears only the pressure of the atmosphere, which is not sufficient to delay very long the separation of the molecules of calcium oxide from the molecules of carbonic acid; on the other hand, in the igneous rocks an enormous pressure must have hindered this decomposition, and have allowed the carbonate of calcium to melt, and subsequently, on cooling, to crystallize.

This theory of Hutton's suggested to James Hall[1] the famous experiment which he communicated in 1804 to the Royal Society of Edinburgh: under sufficient pressure, amorphous calcium carbonate melts without undergoing decomposition, and changes into crystalline marble.

The ideas developed by Lavoisier concerning the resistance which pressure offers to the vaporization of liquids, extended by Hutton to chemical decomposition, found in Dalton[2] an opponent.

In studying the vaporization of a liquid in a closed vessel containing a gas, Dalton shows that, at a given temperature, the same amount of vapor is formed as when the gas is absent, the only difference being that the vapor is formed more slowly. "The presence of the atmosphere", concludes Dalton, "is an obstacle, not to the formation, but to the diffusion of the vapor, which diffusion would take place immediately, as in a vacuum, if the molecules of the air did not prevent it by their inertias. This obstacle is

[1] James Hall. Experiments on whinstone and lava (1798). Nicholson's Journal, **4**, 8, 56 (1801); Trans. Roy. Soc. Edinb. **5**, 43 (1805); Gilbert's Annalen, **7**, 285 (1801); Hoff's Magazine, p. 185 (1801). Experiments on the effects of heat modified by compression. Nicholson's Journal, **9**, 98; Jour. de Phys. **60**, 197; Bull. Soc. philomathique, **3**, 249 (1804). Account of a series of experiments, showing the effects of compression in modifying the action of heat. Nicholson's Journal, **13**, 328, 381 (1806); Trans. Roy. Soc. Edinb. **6**, 71 (1812); Jour. des Mines. **24**, 23 (1808); Jour. de Phys. **64**, 461 (1807).

[2] Dalton. Experimental essays on the constitution of mixed gases; on the force of steam and vapour from water and other liquids at different temperatures, both in a Torricellian vacuum and in air; on evaporation; and on the expansion of gases by heat. Mem. Phil. Soc. Manchester, **5**, 525 (1802); Gilbert's Annalen, **12**, 310, 385; **13**, 438; **15**, 1, 121 (1803); Nicholson's Journal, **3**, 267; **5**, 241 (1802).

the more easily thrust aside as the absolute force of the vapor increases; it is not due to the pressure or to the weight of the atmosphere, as has been believed hitherto, for, if such were the case, no vapor could form above the boiling temperature; but it is an obstacle analogous to that which a stream of water encounters in running through gravel".

Dalton protests vigorously against Lavoisier's assertion that the pressure of the atmosphere alone keeps water, at ordinary temperatures, in the liquid state. "If", he says, "the air in the almosphere were to disappear suddenly, leaving only the water vapor, the latter would increase in quantity but slightly, for the atmosphere already contains very nearly the maximum of vapor which the temperature can produce and maintain; the suppression of the obstacle, however, would hasten the evaporation without sensibly increasing its amount.

"The idea that pressure prevents the evaporation of liquids, an idea which is accepted as an axiom by modern physicists, is perhaps responsible for more mistakes and confusion in science than any other equally erroneous opinion."

Berthollet, an advocate of the ideas of Lavoisier and of Laplace, does not let pass without protest this sweeping criticism. "Dalton's remark", he says,[1] "does not appear to me to be correct, and as a consequence of his opinion it seems to me that he is led to an incorrect estimate of the quantity of vapor which would be formed by the suppression of the atmosphere, and of the amount which can be absorbed by the atmosphere." Nevertheless the clear and logical body of doctrine in which Dalton coordinated the phenomena of vaporization was soon universally accepted. In his *Traité de physique experimentale et théorique*, Biot, who so scrupulously keeps the ideas of Lavoisier and of Laplace on affinity and on the caloric, completely abandons the theory of vaporization developed by Lavoisier; he no longer even mentions the obstacle which pressure by its magnitude alone was supposed to offer to vaporization, while on the other

[1] Berthollet. Essai de Statique chimique, Tome I, p. 491 (1803).

hand he gives a masterly exposition of the theories of Dalton.

What Dalton had established in opposition to the ideas of Lavoisier concerning vaporization, Georges Aimé undertook to repeat for the theory of Hutton. He undertakes to show that, "when a body is decomposed by heat, it is not the pressure of any gas or vapor chosen at random that can stop its decomposition; it is the gas which arises from the decomposition, which alone can act."

Georges Aimé shows, in the first place, that the decomposition of a carbonate by an acid, in a closed vessel, stops when the carbonic acid formed reaches a certain pressure, which depends upon the nature of the carbonate and of the acid used; with carbonate of calcium and dilute hydrochloric acid he finds this pressure to be eight atmospheres. "With sodium carbonate and tartaric acid, the pressure did not exceed seven atmospheres; with acetic acid, the pressure reached six atmospheres; with citric acid the pressure gauge indicated six atmospheres and a half."

The pressure, which stops the decomposition of a given carbonate by a given acid, is fixed. "It might be thought that the pressures obtained depend upon the relative amounts of the substances used or upon their individual masses, considered with reference to the capacity of the vessel. This is how I decided the question: having poured a considerable quantity of acetic acid upon some sodium carbonate, I waited until the pressure gauge became stationary; then I allowed part of the gas to escape, and the pressure gauge returned to the same reading.

"I then varied the quantity of acid and of carbonate; and when these quantities were such that the gas generated by them under atmospheric pressure would have occupied a volume thirty or forty times that of the closed vessel, I found always very nearly the same pressure."

But when, at a definite pressure of the carbonic acid generated by the reaction, the reaction stops, to what should this be attributed? To the magnitude of the pressure, merely, according to Hutton's idea, or to the fact that this pressure is

exerted by the carbonic acid? To decide this dilemma, Georges Aimé establishes, with respect to the pressure of the carbonic acid which stops the reaction, a law similar to the law of the mixture of gases and vapors discovered by Dalton:

"Wishing to know", he says, "if the decomposition of the carbonate is stopped only by the pressure of carbonic acid, or by the pressure of any gas whatever, I placed an acid in a glass bulb terminated by a capillary tube of about the same length as the test-tube. This bulb was placed in the test-tube; I increased the pressure of the air in the tube to three or four atmospheres; I then broke the bulb and the pressure gauge indicated three or four atmospheres more than in the case of the carbonic acid alone. It is, thus, the pressure of the carbonic acid which alone is able to stop the decomposition of the carbonate."

Thus the action of carbonic acid can counterbalance the action of another acid, such as actic acid, upon a base, such as soda, so that these actions equilibrate; for such an equilibrium it is sufficient that the carbonic acid be suitably compressed. "It seems thus to follow from these facts, that the affinity of carbonic acid, suitably compressed, can become equal to that of an organic acid chosen at random, in such wise that the base combines indifferently with the carbonic acid or with the organic acid."

Does the pressure of the carbonic acid which ensures the equilibrium of the system, depend upon the temperature to which the system is raised? Georges Aimé does not put this question to any experimental test and does not even mention it; but if it be noticed that his object is precisely to correct the explanation, given by Hutton's theory, of James Hall's experiment, there can remain no doubt that he tacitly admitted the variation of this pressure with the temperature. In this brief memoir, he leaves to the reader the application of the ideas which result from his experiments, to the fusion of carbonate of calcium under pressure, obtained by the English physicist; but this application admits of no ambiguity, it leads of necessity to the explanation given later by H. Sainte-Claire Deville and Debray.

Although the thesis in which Georges Aimé's observations are recorded is dated 1837, the observations, as the author himself tells us, were communicated to Dumas as early as 1834. It is not until 1864 that Henri Sainte–Claire Deville publishes similar views concerning the influence of pressure upom chemical reactions, and then precisely in connection with James Hall's experiment.

In the course of his earlier researches upon the phenomena of dissociation, H. Sainte–Claire Deville pays attention to the changes which chemical reactions undergo as a consequence of variations of temperature, the influence of pressure upon these reactions do not occupy him in the least. This point of view, entirely different from that of Georges Aimé, is shown clearly by the titles which Sainte–Claire Deville gives to his first publications on dissociation: *De la dissociation ou décomposition spontanée des corps sous l'influence de la chaleur.*[1] *Recherches sur la décomposition des corps par la chaleur et la dissociation.*[2] It is only after 1863 that H. Sainte–Claire Deville takes into account the influence that pressure exerts upon the conditions of chemical equilibrium and that he introduces the idea of dissociation pressure. This idea, to which he is led by the desire to establish a complete analogy between the vaporization of a liquid and the decomposition which a gaseous body, such as water vapor, undergoes through the action of heat, first presents itself in his writings in a somewhat vague and indefinite form.

In his first note *Sur le phénomène de la dissociation de l'eau*,[3] H. Sainte–Claire Deville expresses himself as follows:

"The decomposition of a body is a phenomenon quite similar to the boiling of a liquid, the chief character of which is the fixed temperature at which it takes place under the influence of a source of heat of any intensity whatever, provided the pressure remains constant. To sum up, water vapor cannot resist

[1] Comptes rendus, **45**, 857 (1857).

(1860).

[2] Bibliotheque universelle, Arch. de Genève; nouvelle période, **9**, 54

[3] Comptes rendus, **56**, 195 (1863).

the action of a temperature which increases ten-fold its volume at 0° ; accordingly, it is decomposed."

Then, further on : " The decomposition of a body at a relatively low temperature, the phenomenon of dissociation, corresponds to the vaporization of a liquid at a temperature lower than the boiling-point, and the quantity dissociated at a given temperature will be proportional to the dissociation pressure expressed in millimeters of mercury, as the quantity of vapor formed above a liquid at a given temperature is proportional to the maximum pressure of the vapor."

In his note entitled : *De la dissociation de l' acide carbonique et des densités de vapeur*,[1] H. Sainte–Claire Deville writes :

" I have compared *dissociation* or decomposition below its fixed point to the evaporation of a liquid below its boiling-point, a phenomenon which is necessarily incomplete and of which the amount varies with the temperature and the medium in which it takes place ; and I have called *dissociation pressure* the quantity of a body which is decomposed into its own vapor, compared with the total mass subjected to the action of heat."

In his *Leçons sur la Dissociation*[2] H. Sainte–Claire Deville defines more clearly what he understands by the dissociation pressure of water vapor : " What ", he asks,[3] " is the pressure of the uncombined gases (that is, what we shall call later the dissociation pressure) in the flame of the blow-pipe ? " He finds this pressure to be 426 millimeters at 2500° and he adds : " If I continue my comparison between the phenomena of combination and of condensation, I shall say that the fixed temperature of combination of hydrogen and oxygen, at a pressure of 426 millimeters of mercury, is 2500°, just as the fixed point of condensation or dew point of water vapor is 84.6° at the same pressure of 426 millimeters. We know, moreover, that this dew point is always the same, whether the vapor be alone in a closed vessel or mixed with air or any other gas which does not react with it,

[1] Comptes rendus, **56**, 729 (1863).

[2] Leçons sur la Dissociation, professées devant la Société chimique de Paris, le 18 mars et le 1 avril 1864 (Leçons de la Société chimique de Paris).

[3] loc. cit. Chapitre II.

provided that its pressure be 426 millimeters. In the flame at 2500°, the detonating gas is mixed with water vapor, its pressure is 426 millimeters, the total pressure being 760 millimeters."

Obviously, the notion of dissociation pressure contained in this passage is quite the one which, a few years later, H. Debray,[1] a faithful interpreter of the ideas of H. Sainte-Claire Deville, defined in these terms: "Certain gaseous or volatile compounds are partially and progressively decomposed as the temperature rises. A mixture is then obtained, formed of the gases resulting from the decomposition of the original body, and of that portion of the latter which has not been decomposed, a mixture in which the pressure of the elements separated by heat, constant at a given temperature, increases with that temperature."

We now know that this first example given by Sainte-Claire Deville of a dissociation pressure analogous to the pressure of a saturated vapor, and, like the latter, a function of the temperature alone, was taken from a chemical system which does not possess such a dissociation pressure. The pressure of the gas arising from the dissociation of water which is raised to a given temperature does not depend upon that temperature alone; it changes with the total pressure to which the system is subjected; it changes if an excess of oxygen or of hydrogen is introduced into the system.

Of the analogy which he assumes between the dissociation pressure and the pressure of saturated vapor, and consequently between the temperature of decomposition of a body under a given pressure and the boiling temperature of a substance under a given temperature, Sainte-Claire Deville makes a more fortunate application in showing that it furnishes an explanation of James Hall's experiment. The explanation to which he is led agrees perfectly with the one that follows from the principles established by Georges Aimé. Let us quote the passage[2] in which he gives the explanation of that noted experiment.

[1] H. Debray. Recherches sur la Dissociation. Comptes rendus, **64**, 603 (1867).

[2] loc. cit., Chapitre IV, 6°.

"The famous experiment of James Hall, the fusion of calcium carbonate under pressure, is another phenomenon of the same kind as the best known phenomena of change of state.

"The decomposition of calcium carbonate takes place, like the sublimation of a body, in virtue simply of the action of heat, and changes in two quite distinct ways: 1°. Its fixed point of decomposition, like the boiling-point, rises with the pressure; 2°. In virtue of its dissociation pressure, the amount of decomposition varies with the nature of the gas which, at any moment, is in immediate contact with its molecules. The decomposition of calcium carbonate is like the sublimation of arsenic; but the product of the decomposition is carbonic acid, while arsenic vapor is the product of the sublimation of solid arsenic. It is clear that below its *boiling-point*, if the arsenic is in contact with a layer of its saturated vapor at the temperature of the experiment, the arsenic will no longer sublime, because of its pressure at that temperature. For the same reason, at a given temperature and in a closed vessel, the decomposition of calcium carbonate is only partial, but it will become total if the carbonic acid formed is swept away, as in the experiment of Gay-Lussac. Under the same conditions the solid arsenic will change entirely into vapor. But, if closed vessels be used, the pressure of the carbonic acid or of the arsenic will each raise the point of total decomposition or of total sublimation of the two bodies, and each will reach a temperature at which it can exist in the liquid state."

The researches of Deville left the idea of a dissociation pressure, fixed at each temperature and analogous to the pressure of a saturated vapor, as an hypothesis which no direct experiment justified. H. Debray undertook to transform this hypothesis into an experimental fact, and, for that purpose, he turned[1] to the reaction which, from the time of James Hall, had tried the ingenuity of physical chemists: the decomposition of calcium carbonate by heat.

[1] H. Debray. Recherches sur la dissociation. Comptes rendus, **64**, 603 (1867).

The experimental laws established by H. Debray are the following:

"1°. The dissociation pressure of calcium carbonate is constant at a given temperature. 2°. This pressure increases with the temperature. 3°. It is independent of the state of decomposition of the calcium carbonate."

These laws lead to ideas concerning the influence of pressure upon chemical reactions, which are in all points similar to those which Georges Aimé had formulated thirty years before.

The experiments of Debray give a direct demonstration of two laws which Georges Aimé without doubt tacitly admitted, but which he neglected to verify experimentally, namely:

The dissociation pressure varies with the temperature;

When the pressure of the carbonic acid exceeds the dissociation pressure, instead of the generation of carbonic acid, the absorption of the gas is observed.

Moreover, the experiments of H. Debray dealt directly with the system which James Hall had studied, while the experiments of Georges Aimé dealt with a system in which a more complicated chemical reaction occurs. We now know that if a system contains carbonic acid gas, solid sodium carbonate, solid sodium acetate, and a liquid mixture of these substances in crystallizable acetic acid, the states of equilibrium of the system follow the same laws as the states of equilibrium of a system which contains only carbonic acid, calcium carbonate, and calcium oxide; in the one system as in the other, at a given temperature, equilibrium is reached when the carbonic acid exerts a definite pressure which depends upon the temperature alone. In both cases this pressure may be called by the same name: dissociation pressure of the carbonate. But this assimilation, allowable to-day, of a system in which a carbonate is decomposed by heat with a system in which acetic acid replaces the carbonic acid of a carbonate, might have seemed particularly venturesome at the time when Georges Aimé admitted it without discussion.

Finally, the conditions under which the experiments of Georges Aimé were carried on are not well known, and it is not

easy to decide whether these conditions are really the ones under which the laws formulated by Aimé are applicable.

On the other hand, the experiments of Georges Aimé, more complete in this respect than those of Debray, show that the dissociation pressure is the same in an inert gas as in a vacuum, and their author very properly attributes great importance to this law, analogous to the law of the mixture of gases and vapors discovered by Dalton.

H. Sainte-Claire Deville and H. Debray never knew of the discoveries of Georges Aimé concerning the influence of pressure upon chemical reactions; if they had, with their scrupulous honesty, they would not have failed to mention them. Their ignorance is in no way surprising; when they took up the study of dissociation, Aimé's thesis,[1] the only place in which these ideas had been recorded, had doubtless become very rare, and no voice was raised in support of the claims of their author, long since dead.

In exhuming to-day Aimé's work, we do not mean to diminish in any way the ever-growing fame of H. Sainte-Claire Deville and of H. Debray, inasmuch as this work, unknown to them, can have been of no service to them. But we think it right, hereafter, to place next to their names that of the physicist who, the first, clearly formulated the idea of dissociation pressure; long enough has he remained buried in oblivion — the too frequent fate of thinkers who are in advance of their time.

[1] At its meeting of April 27, 1899, the *Société des Sciences Physiques et Naturelles de Bordeaux* decided that a reprint of Georges Aimé's thesis should be published in its *Mémoires*.

DIFFERENCES OF POTENTIAL BETWEEN METALS AND NON-AQUEOUS SOLUTIONS OF THEIR SALTS

BY LOUIS KAHLENBERG

INTRODUCTION

The osmotic theory of the voltaic cell has led to numerous careful measurements of the differences of electrical potential that exist between metals and the aqueous solutions of their salts in which they are immersed. The measurement of "single potentials" became possible when by means of the so-called dropping electrode one difference of potential between a metal and the solution in contact with it had become established. In the normal calomel electrode, — Mercury | mercurous chloride in normal solution of potassium chloride, — the difference of potential between the metal and the solution has been found to be — 0.56 volt,[1] the minus sign indicating that the metal is positive toward the solution. Many measurements have been made against this normal electrode, using it as a half cell and deducting its value from the total E. M. F. of the combination measured. According to Richards[2] the half cell in which a *n*/10 solution of potassium chloride instead of a normal solution is employed has a more constant potential and investigators are consequently beginning to use the *n*/10 electrode in place of the normal electrode. A few differences of potential between metals and salts in the molten state have recently been measured by Gordon.[3] The contact potential between metals and non-aque-

[1] Compare Ostwald. Zeit. phys. Chem. **1**, 583 (1887). Also some work on single differences of potential by Carveth. Jour. Phys. Chem. **2**, 287 (1898), where the value — 0.56 is regarded as uncertain.

[2] Zeit. phys. Chem. **24**, 39 (1897).

[3] Proc. Am. Acad. **34**, 59 (1898).

ous solutions of their salts has received almost no attention, probably because of the widespread erroneous idea that non-aqueous solutions of salts are generally such poor conductors of electricity as to exclude the possibility of the measurement of the electromotive forces in question.

In 1894 H. C. Jones[1] measured the contact potential between silver and silver nitrate solutions; in the preparation of the latter water, ethyl alcohol, methyl alcohol and acetone were used as solvents. The combinations measured were made up as follows: $Ag|AgNO_3$ in water, $AgNO_3$ in alcohol $|Ag$, methyl alcohol and acetone being used in turn instead of alcohol. The solutions used always contained the same amount of salt per liter. The electrode in the non-aqueous solution was in each case found to be the positive pole of the chain. The highest E. M. F. measured was 0.182 volt, in the case where acetone was used as solvent; when methyl and ethyl alcohol were used, the highest values found were 0.123 volt and 0.130 volt respectively. Now since these non-aqueous solutions of silver nitrate do not conduct electricity as well as aqueous solutions, the former contain fewer ions according to the theory of electrolytic dissociation. If with Nernst it be assumed that the metal has an electrolytic solution tension and that the difference of potential between the metal and the solution is determined by the magnitude of the solution tension and that of osmotic pressure of the silver ions, in the solution, then (if for a moment the assumption be made that the solution tension does not vary when the solvent is changed) the silver in the non-aqueous solution ought to be the negative pole of the above combination. Since experiment shows that the opposite is the case, Jones concludes that the solution tension of silver is different in acetone and alcoholic solutions from what it is in aqueous solutions; in other words, the solution tension of silver is not a constant for all solvents of its salts, but varies with the nature of the solvent in which the silver salts are dissolved. He states that the same will probably be found to be true for other metals also.

Jones discusses the question as to the E. M. F. at the points

[1] Zeit. phys. Chem. **14**, 346 (1894).

where the alcoholic solutions touch the aqueous solutions and also where the two alcoholic solutions come into contact with each other. He found experimentally that while silver in silver nitrate solution in ethyl alcohol is more positive toward the aqueous solution than is silver in silver nitrate solution in methyl alcohol, silver in the latter solution is positive toward silver in the ethyl alcohol solution, — to be sure by less than 0.01 volt. According to Jones this would indicate that a difference of potential exists between the alcoholic solutions at their points of contact. But even if the silver in the ethyl alcohol had been positive toward that in the methyl alcohol, this would not have made it less probable that an E. M. F. exists at the junction of the two solutions. It is well known that the point of contact of two electrolytes is in general the seat of an E. M. F., which, however, on the whole is not great, amounting to only a few hundredths of a volt at most as a rule. The measurements of Jones too would indicate that the E. M. F. at the contact of two solutions is slight.

The object of the present investigation is to determine the differences of electrical potential that exist between metals and various non-aqueous solutions of their salts. While the main object at present is to accumulate facts, the results obtained will also be viewed in the light of the osmotic theory of the galvanic cell as developed by Nernst and Ostwald as far as existing data essential for this purpose will permit. In a previous article[1] the electrical conductivity of a number of non-aqueous solutions was presented. These conductivity measurements have since been continued by Mr. A. T. Lincoln, whose results are ready for publication and will appear shortly in the pages of this journal. The present article contains the results of one of a series of investigations of non-aqueous electrolytic solutions that is in progress in this laboratory.

Method of Experimentation and Materials Employed. — The electromotive forces were measured by means of the compensation method of Poggendorf, using a Lippmann's electrometer as a zero instrument.[2] The latter was sufficiently sen-

[1] Kahlenberg and Lincoln. Jour. Phys. Chem. 3, 12 (1899).

[2] Compare Ostwald, Hand- und Hilfsbuch, 254.

sitive to permit measurements to be made to one millivolt. In a few cases, however, where the solutions were very poor conductors of electricity this degree of accuracy was not quite attained.

A Leclanché cell was used as the "working element" in the compensation process. The E. M. F. of this Leclanché cell was determined before and after each measurement by means of a Helmholtz one volt element; the latter was in turn compared at times with a Clark element and also with a Weston element. The three standard elements showed excellent agreement throughout the investigation, and the E. M. F. of the Leclanché cell also became remarkably constant after a time.

In a number of cases measurements were made directly against a normal calomel electrode, the E. M. F. of which was assumed to be —0.56 volt. In fact all the "single potentials" given below are calculated on this value of the normal electrode as a basis. A *n*/10 calomel electrode was also prepared. It was connected with the normal electrode and the E. M. F. of the combination was found to be 0.053 volt. Although the measurement was repeated at various times the same result was always obtained. A student in this laboratory, who had independently prepared two of these electrodes, also obtained 0.053 volt on measuring the E. M. F. of the electrodes when combined. This makes the value of the *n*/10 electrode —0.613 volt, the E. M. F. at the contact of the *n*/1 and *n*/10 solutions being disregarded in making the calculation.

The general arrangement of the voltaic combinations measured was as follows: The metals dipped into solutions contained in test-tubes or small beakers placed on a level and filled to the same height. The connection between the two vessels was made by means of a strip of good filter-paper folded to several thicknesses; thus the solutions soaked into the filter-paper from each end, and when the liquids met in the pores of the paper near the middle of the strip the electrical connection was established and the measurement could be made without much danger of either of the solutions passing over into the other dish. As with but

few exceptions the metals dipped into solutions of their salts, the E. M. F. was as a rule quite constant and the measurement occupied only a few moments in each case. The use of the strip of filter-paper, besides offering the advantage mentioned, enabled me to work with smaller quantities of solutions than could very well have been used if the connection between the two half cells had been made in the usual way by means of a ∩ tube filled with one of the solutions. This was important as but small quantities of the solvents were available in some cases. I assured myself by experiment that the results obtained by the method adopted were not appreciably different from those that were found when the connection was made by means of the ∩ tube in the usual way.

Unless otherwise stated the solvents used were perfectly anhydrous. All of them were of standard manufacture, having been obtained from either Kahlbaum, Schuchardt, Merck or Trommsdorff. In a few cases I prepared and purified the solvents myself as they were not on hand and could not be secured in this country.

The salts employed were of the C. P. variety. They were carefully dehydrated after preparation, or they were prepared in anhydrous form at the outset. The solutions were prepared by dissolving a weighed quantity of salt (with the aid of heat when necessary) and diluting the resulting solution to the volume desired. The solutions of the anhydrous nitrates of zinc, magnesium, copper, cadmium and thallium in pyridine and aniline were obtained by treating $n/10$ solution of silver nitrate with each of these metals; thus silver was thrown out and the solution of the nitrate desired was at once obtained. These metals were allowed to remain in contact with the solutions till no more silver was precipitated, and till other analytical tests showed that silver was no longer present. In all cases the silver nitrate solution was allowed to remain in contact with an excess of the respective metals for two or three weeks, in some cases (particularly those of magnesium and zinc) for months. The precipitation of the silver generally begins to become apparent as soon as

the other metal is brought into contact with the solution, but the last traces of silver require considerable time for their removal. It suggested itself that the process could be hurried by electrolyzing the silver nitrate solution, using the metal whose nitrate is desired as anode. In the case of the pyridine solution, the liquid turned dark even when a weak current was employed, and so it was decided not to use this method, for it was evident that some secondary change was taking place. The following metals completely replace silver in a silver nitrate solution in pyridine: magnesium, zinc, cadmium, thallium, lead, copper. Mercury seems to replace silver only partially, while iron, nickel, cobalt, aluminum, gold and platinum may remain a long time in the silver nitrate solution without any visible change, their surfaces remaining perfectly bright. The solution of silver nitrate in aniline behaves in an analogous manner toward the metals mentioned. In the case of this solution it was also ascertained that tin, antimony and bismuth do not precipitate the silver. Whether the fact that the metals above named do not replace silver in these solutions is to be explained by the sparing solubility of their nitrates — which would have to form — has not been determined. It is easy to see why gold and platinum should not replace silver, but the behavior of the other metals is not so readily explained. This matter will be taken up again in connection with another investigation.

The electrodes used were in the form of sticks or foil. They were of the purest metals obtainable in the market. The electrodes were carefully cleaned with emery cloth until their surfaces were bright. They were then washed with water and dried with clean filter-paper. The electrodes were thus cleansed before each determination; and neither the emery cloth nor the filter-paper was used more than once, new pieces being employed each time so as to guard against contamination of the surfaces of the metals. In those voltaic chains in which both electrodes were of the same metal, special care was taken to test the electrodes in one and the same solution to see whether they were alike; and, as a rule, the electrodes used in the chain were ex-

changed after being washed and wiped with clean new filter-paper — and the E. M. F. of the combination was then measured again. The results so obtained always agreed to a millivolt. The measurements were in all cases made at room temperature, about 20° C.

Presentation of Results. — Silver nitrate dissolves in a relatively large number of solvents yielding solutions that conduct electricity. Twenty-four $n/10$ solutions were prepared, a different solvent being used in each case, and the differences of potential between these solutions and metallic silver dipping into them were determined. The number of different solvents used in preparing the solutions of salts of other metals is not as great.

In the calculation of so-called single or absolute potentials, the E. M. F. at the contact of the liquids has throughout been disregarded. These electromotive forces are as a rule small, but in some cases they amount to several hundredths of a volt. An examination of the results given below will show this so that further comment on this point seems unnecessary. An experimental determination of these electromotive forces has thus far not been attempted because they are of secondary importance, and because, in many cases at least, the rather complicated chains necessary in making such determinations would make it very difficult to obtain sufficiently accurate results because of the high resistance of the solutions.

As stated above, all the absolute potentials given are referred to that of the normal calomel electrode as being -0.56 volt, but measurements were not always made directly against this electrode. A $n/10$ solution of silver nitrate in pyridine being a good conductor, the difference of potential between it and silver could be measured accurately. It was found to be -0.573 volt. Many of the combinations, particularly those made with solutions whose solvents do not mix with water or are but slightly soluble in water, were measured against silver dipping in a $n/10$ solution of silver nitrate in pyridine and the single potentials sought were then calculated. In a few cases measurements were made using silver in $n/10$ aqueous solution of silver nitrate as a

half cell — whose E. M. F. was ascertained to be —1.018 volts — and the single potentials were calculated from the results obtained. To ascertain a single potential, i. e. the E. M. F. of a half cell, the latter was connected successively with two or more half cells of E. M. F. of the combination previously ascertained ; the total E. M. F. formed was then measured and the single potential sought calculated in each case. This course was taken in order that the separate determinations might act as a check the one upon the other.

The results of the measurements are given in the following table. The combinations are numbered in the first column in order to facilitate future reference to them. The second column gives in detail the voltaic chains measured. The common way of writing them has been adopted so that further explanations will not be necessary. A plus sign indicates the positive pole of the chain. All solutions contain one-tenth of a gram equivalent of salt per liter unless otherwise indicated. Where no mention of the salt contained in the solution is made, silver nitrate was used. The solvents are given in all cases. The third column contains the E. M. F. of the total combination, and the fourth column contains the absolute E. M. F. of the *first half* of the chain, the calculation being made as already explained. In all cases the electromotive forces are given in volts.

No.	Voltaic Chain	E. M. F.	Absolute E. M. F.
1	$\overset{+}{Ag}$ | Water | N. electrode	0.458 V	—1.018 V
2	$\overset{+}{Ag}$ | Water | Pyridine | Ag	0.419	—0.992
3	$\overset{+}{Ag}$ | Methyl alcohol | Water | Ag	0.090[1]	—1.108
4	$\overset{+}{Ag}$ | Ethyl alcohol | N. electrode	0.532	—1.083
5	$\overset{+}{Ag}$ | Ethyl alcohol | Water | Ag	0.092[2]	—1.110
6	$\overset{+}{Ag}$ | Ethyl alcohol | Pyridine | Ag	0.569	—1.142
7	$\overset{+}{Ag}$ | Allyl alcohol | Water | Ag	0.065	—0.953
8	Ag | Allyl alcohol | Ethyl alcohol | $\overset{+}{Ag}$	0.150	—0.963

[1] Taken from the work of Jones (l. c.).

[2] Jones (l. c.) found 0.095 volt for this chain.

No.	Voltaic Chain	E. M. F.	Absolute E. M. F.
9	Ag^{+} | Allyl alcohol | Pyridine | Ag	0.423	—0.996
10	Ag^{+} | Benzyl alcohol | Water | Ag	0.026	—0.992
11	Ag | Benzyl alcohol | Ethyl alcohol | Ag^{+}	0.052	—1.058
12	Ag^{+} | Benzyl alcohol | Pyridine | Ag	0.531	—1.104
13	Ag | Glycol | Water | Ag^{+}	0.002	—1.016
14	Ag | Glycol | Ethyl alcohol | Ag^{+}	0.097	—1.013
15	Ag^{+} | Glycol | Pyridine | Ag	0.424	—0.997
16	Ag | Glycerine | Water | Ag^{+}	0.039	—0.979
17	Ag | Glycerine | Ethyl alcohol | Ag^{+}	0.114	—0.996
18	Ag^{+} | Glycerine | Pyridine | Ag	0.350	—0.923
19	Ag^{+} | Acetone | N. electrode	0.608	—1.168
20	Ag^{+} | Acetone (Sat. sol.) | Pyridine | Ag	0.613	—1.196
21	Ag^{+} | Acetonitrile (Sat. sol.) | N. electrode	0.302	—0.862
22	Ag^{+} | Acetonitrile | Pyridine | Ag	0.370	—0.943
23	Ag | Benzonitrile | Water | Ag^{+}	0.013	—1.005
24	Ag^{+} | Benzonitrile | Pyridine | Ag	0.445	—0.982
25	Ag | Ethyl cyanacetate | Pyridine | Ag	0.482	—1.055
26	Ag | Pyridine | N. electrode	0.013	—0.573
27	Ag | Pyridine | N/10 electrode	0.039	—0.574
28	$N/10^{+}$ electrode | N. electrode	0.053	—0.613
29	Ag^{+} | Quinoline | Pyridine | Ag	0.044	—0.617
30	Ag | Piperidine | N. electrode	0.088	—0.472
31	Ag | Piperidine | Pyridine | Ag^{+}	0.151	—0.422
32	Ag | Aniline | Pyridine | Ag	0.169	—0.742
33	Ag | Methylaniline[1] | Pyridine | Ag	0.417	—0.990
34	Ag^{+} | Dimethylaniline[1] | Pyridine | Ag	0.352	—0.925
35	Ag^{+} | o. Toluidine | Pyridine | Ag	0.156	—0.729

[1] These solvents did not yield clear solutions of silver nitrate; reduction apparently takes place to some extent.

No.	Voltaic Chain	E. M. F.	Absolute E. M. F.
36	Ag | m. Xylidine 1.3.4. | Pyridine | Ag	0.169	—0.742
37	Ag | n. Propylamine | Water | Ag	0.622	—0.396
38	Ag | n. Propylamine | Pyridine | Ag	0.212	—0.361
39	Ag | n. Butylamine | Water | Ag	0.605	—0.413
40	Ag | n. Butylamine | Pyridine | Ag	0.203	—0.370
41	Ag | iso-Butylamine | Pyridine | Ag	0.178	—0.395
42	Ag | iso-Butylamine | Water | Ag	0.575	—0.443
43	Ag | Amylamine | Water | Ag	0.576	—0.442
44	Ag | Amylamine | Pyridine | Ag	0.196	—0.379
45	Ag | mono-Benzylamine | Pyridine | Ag	0.186	—0.391
46	Ag | AgCN in Pyridine | Pyridine | Ag	0.054	—0.519
47	Mg | $Mg(NO_3)_2$ in Pyridine | N. electrode	0.984	+0.424
48	Mg | $Mg(NO_3)_2$ in Pyridine | Pyridine | Ag	0.929	+0.356
49	Mg | $Mg(NO_3)_2$ in Aniline | Aniline | Ag	1.151	+0.409
50	Zn | $ZnCl_2$ in Water | N. electrode	1.082	+0.522
51	Zn | $ZnCl_2$ in Pyridine | N. electrode	0.832	+0.272
52	Zn | $ZnCl_2$ in Water | $ZnCl_2$ in Pyridine | Zn	0.274	+0.546
53	Zn | $Zn(NO_3)_2$ in Pyridine | N. electrode	1.079	+0.519
54	Zn | $Zn(NO_3)_2$ in Pyridine | $ZnCl_2$ in Water | Zn	0.026	+0.496
55	Zn | $Zn(NO_3)_2$ in Pyridine | $ZnCl_2$ in Pyridine | Zn	0.234	+0.506
56	Zn | $Zn(NO_3)_2$ in Pyridine | Pyridine | Ag	1.087	+0.514
57	Zn | $ZnCl_2$ in Aniline | $ZnCl_2$ in Pyridine | Zn	0.111	+0.383
58	Zn | $Zn(NO_3)_2$ (Saturated solution) in Aniline | Aniline | Ag	0.916	+0.174
59	Zn | $ZnCl_2$ (Saturated solution) in Quinoline | N. electrode	0.494	—0.066
60	Zn | $ZnCl_2$ in Quinoline | $ZnCl_2$ in Water | Zn	0.598	—0.076

No.	Voltaic Chain	E. M. F.	Absolute E. M. F.
61	Zn | $ZnCl_2$ in Ethyl alcohol | N. electrode	0.910	+0.350
62	Zn | $ZnCl_2$ in Ethyl alcohol | $ZnCl_2$ in Water | Zn	0.195	+0.327
63	Cd | $Cd(NO_3)_2$ in Pyridine | N. electrode	0.785	+0.225
64	Cd | $Cd(NO_3)_2$ in Pyridine | Pyridine | Ag	0.746	+0.173
65	Cd | $Cd(NO_3)_2$ in Pyridine | $Zn(NO_3)_2$ in Pyridine | Zn	0.340	+0.179
66	Tl | $TlNO_3$ in Pyridine | Pyridine | Ag	0.699	+0.126
67	Pb | $Pb(NO_3)_2$ in Pyridine (0.1557 g in 10 cc) | N. electrode	0.297	−0.263
68	Pb | $Pb(NO_3)_2$ in Pyridine | N. electrode	0.203	−0.357
69	Pb | $Pb(NO_3)_2$ in Pyridine | Pyridine | Ag	0.170	−0.403
70	Pb | $Pb(NO_3)_2$ in Aniline | Aniline | Ag	0.327	−0.415
71	Cu | $Cu(NO_3)_2$ in Pyridine (Saturated solution) | Pyridine | Ag	0.366	−0.237
72	Cu | $Cu(NO_3)_2$ in Aniline | Aniline | Ag	0.210	−0.532
73	Cu | $CuSO_4$ in Methyl alcohol (Saturated solution) | N. electrode	0.156	−0.716
74	Sb | $SbCl_3$ in Methyl alcohol (14.5 percent solution) | N. electrode	0.086	−0.489
75	Sb | $SbCl_3$ in Ethyl alcohol (1 mol in 8113 cc) | N. electrode	0.041	−0.519
76	Sb | $SbCl_3$ in Methyl alcohol (14.5 percent solution) | $SbCl_3$ in Ethyl alcohol (1 mol in 8113 cc) | Sb	0.013	−0.506
77	Sb | $SbCl_3$ in Methyl alcohol (14.5 percent solution) | $CuSO_4$ in Methyl alcohol (Saturated solution) | Cu	0.213	−0.503
78	Sb | $SbCl_3$ in Nitrobenzene (1 mol in 1825.5 cc) | N. electrode	0.181	−0.741
79	Sb | $SbCl_3$ in Nitrobenzene (1 mol in 1825.5 cc) | $SbCl_3$ in Ethyl alcohol (1 mol in 8113 cc) | Sb	0.233	−0.752
80	Bi | $BiCl_3$ in Methyl alcohol (9 percent solution) | N. electrode	0.039	−0.521
81	Bi | $BiCl_3$ in Methyl alcohol (9 percent solution) | $SbCl_3$ in Methyl alcohol (14.5 percent solution) | Sb	0.026	−0.515
82	Fe | $FeCl_2$ in Water (1/10 mol per liter) | N. electrode	0.529	−0.031

No.	Voltaic Chain	E. M. F.	Absolute E. M. F.
83	$\overset{+}{Pt}$ | $FeCl_3$ in Water (1/10 mol per liter) | N. electrode	0.481	—1.041
84	$\overset{+}{Fe}$ | $FeCl_3$ in Ethyl alcohol (1/8 mol per liter) | $FeCl_3$ in Water (1/10 mol per liter) | Fe	0.273	—0.303
85	Pt | $FeCl_3$ in Ethyl alcohol (1/8 mol per liter) | $FeCl_3$ in Water (1/10 mol per liter) | $\overset{+}{Pt}$	0.084	—0.957
86	$\overset{+}{Fe}$ | $FeCl_3$ in Nitrobenzene (1.4508 g in 77.6 cc) | $FeCl_3$ in Ethyl alcohol (1/8 mol per liter) | Fe	0.909	—1.212
87	$\overset{+}{Pt}$ | $FeCl_3$ in Nitrobenzene (1.4508 g in 77.6 cc) | $FeCl_3$ in Ethyl alcohol (1/8 mol per liter) | Pt	0.792	—1.749
88	$\overset{+}{Fe}$ | $FeCl_3$ in o. Nitrotoluene (0.1473 g in 10 cc) | $FeCl_3$ in Ethyl alcohol (1/8 mol per liter) | Fe	0.571	—0.874
89	$\overset{+}{Pt}$ | $FeCl_3$ in o. Nitrotoluene (0.1473 g in 10 cc) | $FeCl_3$ in Ethyl alcohol (1/8 mol per liter) | Pt	0.623	—1.580

It appears from the above table that the single potential of a metal toward a solution varies somewhat according as the measurement is made directly against the normal electrode or against some other half cell, which has been determined directly by measurement against the normal electrode. It will be noticed that these variations affect the second decimal place; they are due to the E. M. F. at the junction of the solutions, which were neglected in calculating the single potentials as stated above.

Discussion of Results. — When the foregoing results are regarded without reference to theory the following facts become evident.

Silver is positive toward all the solutions in which it was tested (Nos. 1 to 45). It is most positive toward the solution in acetone and least toward that in propylamine. The contact-potentials of silver and the aqueous and alcoholic solutions — including glycerine and glycol — (Nos. 1 to 18) are of the same general order, the differences being only a few hundredths of a volt.

While silver is more positive toward the solution in acetone (Nos. 19 and 20) than toward aqueous or alcoholic solutions, it is more positive toward the latter than toward the solution in acetonitrile (No. 21). Toward the benzonitrile solution (Nos. 23 and 24) and also toward the solution in ethyl cyanacetate silver is about as positive as toward the aqueous and alcoholic solutions. Toward the solution in pyridine (Nos. 26 and 27) silver is only about one-half as positive as toward the alcoholic solution. While this metal is slightly more positive toward the solution in quinoline (No. 29) than toward the solution in pyridine, it is less positive toward the solution in piperidine (Nos. 30 and 31) than toward the latter. The contact-potential between silver and the solution in aniline (No. 32) is the same as that between this metal and the solutions in *m*-xylidine (No. 36) and *o*-toluidine (No. 35), the variation in the case of the latter being in the third decimal place. It will be noted that the last three solvents mentioned are closely related in that each contains an amido group in place of one of the hydrogens of the benzene ring. Toward the solutions in methyl- and dimethylaniline (Nos. 33 and 34) silver is about as positive as toward the solutions in glycol (No. 15) and glycerine (No. 18) respectively. Toward the solutions in *n*-butyl, isobutyl, amyl and benzyl amine (Nos. 37 to 45) silver is less positive than toward any of the other solutions except possibly that in piperidine. While the E. M. F. at the contact of silver and the solutions in these amines is of the same general order, it seems from a comparison of Nos. 37, 39 and 43 or Nos. 38, 40, 44 and 45, that the metal becomes more positive toward the solutions in the amines that are higher in the homologous series or are richer in carbon content. A comparison of Nos. 39 and 40 with Nos. 42 and 41 respectively shows that silver is slightly more positive toward the solution in isobutyl amine than toward that in *n*-butyl amine. Silver is somewhat less positive toward a solution of silver cyanide in pyridine than toward one of silver nitrate in the same solvent as No. 46 shows. From an inspection of Nos. 1 to 45, it appears that contact-potentials between a metal and solutions in various

solvents, each containing the same quantity of a salt of the metal per liter, depend on the chemical nature of the solvents; in the case of solvents of a similar chemical nature these differences of potential are approximately the same, this approximation being the better the more closely the solvents are related to one another.

Magnesium is much less negative toward solutions of magnesium nitrate in pyridine and aniline (Nos. 47 to 49) than it is toward an aqueous solution of this salt. Neumann[1] found the E. M. F. at the contact of magnesium and an aqueous, normal solution of magnesium nitrate to be + 1.060 volts. The electromotive force at the contact of magnesium and the aniline solution differs but slightly from that at the contact of this metal and the pyridine solution. It is interesting to note that while silver is less positive toward solutions in aniline and pyridine than toward the aqueous solution, magnesium is more positive (or less negative) toward the former than toward the latter. In other words, this would indicate that silver and magnesium lie closer together in the electrochemical series when pyridine and aniline solutions are under consideration than when aqueous solutions are considered.

Zinc is less negative (or more positive) toward zinc chloride in pyridine (No. 51), aniline (No. 57), quinoline (Nos. 59 and 60), and alcohol (Nos. 61 and 62) than toward the aqueous solution (No. 50). Its behavior is then similar to that of magnesium and hence opposite to that of silver. Toward the solution of zinc nitrate in pyridine (Nos. 53 to 56), zinc is approximately as negative as toward the aqueous solution[2] (No. 55 also 53 and 50); but toward the solution of this salt in aniline the metal is far less negative than toward the aqueous solution[2] (No. 58). The contact-potential of zinc in zinc chloride in quinoline is slight and is in the sense that the metal is positive toward the solution

[1] Zeit. phys. Chem. **14**, 229 (1894).

[2] The contact-potentials between zinc and aqueous solutions of its chloride and nitrate are not very different. Neumann (l. c.) found them to be + 0.503 volt and + 0.473 volt respectively for normal solutions.

(Nos. 59 and 60). This is very unusual, and it is to my knowledge the first case found where zinc is positive toward the solution in which it is immersed. It may be well to state in this connection that, judging from the movements of the mercury of the electrometer the solution of zinc nitrate in pyridine conducts well, the corresponding solution in aniline conducts poorly. The solutions of zinc chloride in pyridine, quinoline and aniline are poor conductors; the alcoholic solution conducts somewhat better.

Cadmium is somewhat more negative toward a solution of cadmium nitrate in pyridine than toward a solution of this salt in water (Nos. 63 to 65). Neumann[1] found the E. M. F. at the contact of this metal and a normal aqueous solution of its nitrate to be + 0.122 volt.

The single case in which thallium was used (No. 66) would indicate that this metal is negative toward a pyridine solution of its nitrate to an extent not very different from what its potential is toward an aqueous solution. Neumann[1] found the E. M. F. at the contact of thallium and a normal, aqueous solution of its nitrate to be + 0.112 volt.

Lead is much more positive toward lead nitrate solutions in pyridine and aniline (Nos. 67 to 70) than toward the aqueous solution of this salt, Neumann[1] having found — 0.115 volt to be the E. M. F. at the contact of this metal and a normal aqueous solution of its nitrate. Lead then behaves toward the pyridine solution of its nitrate in a manner opposite to that in which silver acts toward a solution of its nitrate in this solvent.

Copper is probably somewhat less positive toward the solution of its nitrate in aniline (No. 72) than toward the aqueous solution of this salt. Neumann's[2] value for the E. M. F. at the contact of copper and a normal aqueous solution of its nitrate is — 0.615 volt. Copper is certainly much more positive toward the solution of its sulphate in methyl alcohol (No. 73) than toward the aqueous solution of this salt. Neumann[2] found — 0.515 volt

[1] l. c.
[2] l. c.

for the E. M. F. at the contact of copper and a normal aqueous solution of its sulphate. Toward the pyridine solution of its nitrate (No. 71) copper is probably less positive than toward the corresponding aqueous solution. The saturated solution of copper sulphate in methyl alcohol conducts very poorly.

Towards solutions of antimony trichloride in methyl and ethyl alcohols, antimony is fairly strongly positive (Nos. 74 and 77). These results cannot be compared directly with an aqueous solution of antimony trichloride for the latter dissolves in water only in presence of an excess of acid. Toward the solution in nitrobenzene (Nos. 78 and 79) antimony is much more positive than toward the alcoholic solutions. The alcoholic solutions conduct better than do those in nitrobenzene.[1]

Bismuth is positive toward solutions of its trichloride in ethyl and methyl alcohol (Nos. 80 and 81) to approximately the same extent that antimony is positive toward the solutions of its trichloride in these solvents.[2]

Toward ferric chloride solutions in alcohol, nitrobenzene and orthonitrotoluene iron is much more positive than toward the solution of this salt in water (compare Nos. 82, 84, 86 and 88). Platinum is more positive toward an aqueous than toward an alcoholic solution of ferric chloride (Nos. 83 and 85); but toward solutions of this salt in nitrobenzene and orthonitrotoluene (Nos. 87 and 89) it is much more positive than toward the aqueous solution. The study of the so-called oxydation and reduction chains in which solvents other than water are used is evidently full of interest. It will receive more attention in the future. The few measurements here given are of course entirely insufficient to make any general statements.

I desire here once more to call special attention to the fact that, while the E. M. F. at the contact of a metal and a solution

[1] Compare Kahlenberg and Lincoln, l. c.

[2] Neumann (l. c.) found the E. M. F. at the contact of antimony and antimony trichloride in water plus hydrochloric acid to be −0.376 volt, and at the contact of bismuth and the acidified aqueous solution of its trichloride he determined the E. M. F. to be −0.315 volt.

of its salt varies with the nature of the solvent, this variation may differ, not only as to degree but also as to sense or direction, from the potential that the metal exhibits toward, for example, an aqueous solution of the salt. The results upon which this statement is based have just been discussed in detail and hence it is unnecessary to consider them again here.

The results viewed in the light of the osmotic theory of the cell. — When a metal dips into an aqueous solution of one of its salts the difference of potential between it and the solution may be calculated according to the formula :

$$\pi = \frac{RT}{n_e e_o} \log_{nat} \frac{P}{p},^{1}$$

where π is the difference of potential in volts, R the gas constant so-called, T the absolute temperature, n_e the valence of the metal, e_o the constant of Faraday's law, and P and p the electrolytic solution tension of the metal and the osmotic pressure of its ions in the solution respectively. At a given temperature $\frac{RT}{e_o}$ is a constant; at room temperature (20° C) the formula becomes $\pi = \frac{0.0581}{n_e} \log \frac{P}{p}$, when the common instead of the natural logarithm is used. For a given metal n_e is also a constant, and hence the value of π depends upon the ratio of the solution tension, P, to the osmotic pressure of the metallic ions, p. As the constant of Faraday's law is involved in this formula, it is necessary before attempting to apply the same to non-aqueous solutions to inquire whether Faraday's law holds for the latter. On this point I desire to say, that I have electrolyzed a number of the non-aqueous solutions mentioned above, having a silver voltameter in the same circuit, and the amounts of the metals deposited in the various cases tested show that Faraday's law holds for these solutions as for aqueous solutions. The results of this special investigation will be published in another article.

Now the electrolytic solution tension, P, is a hypothetical

[1] Compare for instance LeBlanc's Elektrochemie, 124.

quantity and can only be found by use of the above formula when π and p are known. As π is readily measured, and as the values of it are given above for a number of combinations — in which non-aqueous solutions are employed — with a degree of approximation sufficient for most purposes, the osmotic pressure of the ions of the metal or p only needs to be ascertained in each case in order that the solution tension of the metal or P may be calculated. To ascertain p it is necessary to determine the degree of electrolytic dissociation of the salt in the solution.

It would be exceedingly interesting to calculate these values of P of the metals toward various solvents, and to see whether the metals have the highest electrolytic solution tension toward those solvents in which their salts conduct best, and whether these solution tensions increase with the dielectric constants of the solvents, etc.

In the case of aqueous solutions of electrolytes the degree of dissociation, a knowledge of which is necessary in order to ascertain p, may be determined from the electrical conductivity according to the well-known formula, $a = \frac{\mu_v}{\mu_\infty}$, where a is the degree of dissociation and μ_v and μ_∞ are the molecular conductivities at the volume v and at infinite dilution respectively. The degree of dissociation can generally also be found by means of the freezing-point or boiling-point methods. In the case of the non-aqueous solutions in question, however, the degree of dissociation cannot be calculated from the electrical conductivity, because μ_∞ is not known.[1] The molecular conductivity of non-aqueous solutions as a rule increases with the dilution but not very rapidly, only rarely do the values found clearly tend toward a maximum. (Compare for example the work of Kahlenberg and Lincoln (l. c.) and the references there given.) To be sure there are also many aqueous solutions that conduct but feebly and yet the value of μ_∞ for them has been found by calculation making use of the fact discovered by Kohlrausch that the conductivity

[1] For silver nitrate in acetonitrile Dutoit and Friderich, Bull. Soc. Chim. Paris. 19, 327 (1898) place μ_∞ equal to 160. This figure will be used below.

in the case of aqueous solutions is an additive property. But for the non-aqueous solutions here in question it has not been established that their electrical conductivity is additive in character. Again the molecular conductivity of some non-aqueous solutions practically does not change with the dilution, though because of the low value of the conductivity and because of the molecular weight of the substance in solution dissociation cannot be considered to be complete.[1] Furthermore, there have been found cases where the molecular conductivity diminishes as the dilution increases.[2] These facts are not in harmony with the theory of electrolytic dissociation.

The question arises, cannot the degree of dissociation in the case of non-aqueous conductivity solutions be found by the freezing-point or boiling-point methods? When the conductivity of the solutions is slight these methods are not sufficiently delicate to detect with certainty the fact that dissociation exists, much less can they be used to estimate the extent of the latter; but when the solutions conduct fairly well these methods certainly ought to enable one to ascertain the extent of the dissociation of the dissolved salt. Dutoit and Friderich[3] have found that the salts $CNSNH_4$, $HgCl_2$, NaI, LiCl, CdI_2 conduct when dissolved in acetone and that they have normal molecular weights in this solvent according to boiling-point determinations. Again ferric chloride in nitrobenzene conducts and the cryoscopic method yields molecular weights increasing with the dilution, all of them being above the theoretical value.[4] A. Werner[5] has found that the molecular weight of silver nitrate in pyridine is practically normal and experiments performed in this laboratory recently have practically confirmed his determinations; nevertheless, Mr. Lincoln, who at my suggestion measured the conductivity of silver nitrate in pyridine solutions, found it to be from one-third

[1] Compare Kahlenberg and Lincoln, l. c.; also Dutoit and Friderich, l. c.

[2] Compare Kahlenberg and Lincoln, l. c.; also Hans Euler. Zeit. phys. Chem. **28,** 619 (1899).

[3] l. c.

[4] Kahlenberg and Lincoln. l. c.

[5] Zeit. anorg. Chem. **15,** 1 (1897).

to one-fourth that of the corresponding aqueous solutions. As the latter conduct well (the dissociation in *n*/10 solution of silver nitrate in water is about 80 percent) the dissociation of the silver nitrate in pyridine ought certainly to be capable of measurement by means of the boiling-point method; the relatively high boiling-point constant (30.07) of pyridine too lends emphasis to the latter statement. We have in a solution of silver nitrate in pyridine a fairly good conductor of electricity with a molecular weight so nearly normal that the conductivity cannot be accounted for by means of the dissociation hypothesis.[1] Werner[2] has also found the molecular weight of silver nitrate in benzonitrile to be normal. While according to determinations made by Mr. Lincoln these solutions conduct only about one-fourth as well as do the pyridine solutions, yet, considering the high boiling-point constant of benzonitrile (36.55), it would seem that even here the boiling-point method ought to yield molecular weights that are less than normal.

From the facts here presented it seems clear that solutions may conduct electricity fairly well and yet the dissolved substance may possess a normal molecular weight, i. e. it may be undissociated. But this point once established, the question arises, cannot conduction then in all solutions be explained without assuming electrolytic dissociation? To be sure then the high osmotic pressure and the correspondingly low molecular weights found in so many cases, in aqueous solutions of electrolytes for instance, would have to be accounted for otherwise than by the dissociation hypothesis. It is not my purpose to enter upon this matter in this connection. What has been said is sufficient to indicate that the data necessary to calculate the degree of dissociation of the salts in the non-aqueous solutions used in the above galvanic chains are not at hand, and that in cases

[1] The high electrical conductivity of salts in liquid ammonia (Cady, Jour. Phys. Chem. **1**, 712 (1897)), and the boiling-points of such solutions (Franklin and Kraus, Am. Chem. Jour. **20**, 848 (1898)), are of interest in this connection.

[2] l. c.

where the electrical conductivity or the molecular weight or both are known it is still not possible to get at the extent of the dissociation. Indeed as has been stated, the behavior of some of the solutions is such that it seems clear that while they do conduct, yet the dissolved salt is undissociated and hence it seems like hunting the will-o-the-wisp to seek to ascertain the degree of dissociation in such cases.

It appears then from what has been said that the p of the above formula is not obtainable and consequently the solution tensions of the metals toward the various solvents cannot be calculated. There is apparently one exception to this which has been alluded to in a foot-note above. Silver nitrate when dissolved in acetonitrile conducts well, in fact better[1] than when dissolved in water. Dutoit and Friderich[2] place μ_∞ for silver nitrate in acetonitrile equal to 160; though why they choose this figure is not quite evident, since their results show that the conductivity increases regularly with the dilution, the last four determinations indicating no tendency toward a maximum. But if 160 be taken as the value of μ_∞, the degree of dissociation in a $n/10$ solution is about 36.7 percent. The p of the above formula then becomes 0.367 of the osmotic pressure of one gram-ion contained in ten liters. At 20° C the osmotic pressure of one gram-ion in ten liters is 2480.2 grams or 1.9513 atmospheres per sq. cm. Substituting in the formula then we have,

$$-0.862^3 = 0.0581 \log \frac{P}{1.9513 \times 0.367},$$

whence $P = 1.04 \times 10^{-15}$ atmospheres. If a similar calculation is made for the aqueous solution, assuming the degree of dissociation in $n/10$ solution to be 82.1 percent, we have,

$$-1.018^4 = 0.0581 \log \frac{P}{1.9513 \times 0.821},$$

[1] At higher dilutions.

[2] l. c.

[3] Taken from measurement No. 21, above.

[4] Taken from No. 1, above.

whence $P = 4.82 \times 10^{-18}$ atmospheres. Thus it appears that the solution tension of silver toward acetonitrile is greater than toward water. This harmonizes with the fact that in dilute solutions silver nitrate conducts better in acetonitrile than in water, though this difference may, at least in part, be due to the fact that water is more viscous than acetonitrile. The dielectric constant of acetonitrile has not been determined, to my knowledge, so that a comparison of the solution tensions toward the two solvents with the dielectric constants of the latter cannot be made.

If it be assumed that silver nitrate in pyridine is dissociated to one-fourth the extent that it is in water (an assumption that is open to strong objections) because in the former solutions its conductivity is about one-fourth that in the latter, we have the following upon substituting the proper values in the formula,

$$-0.573^{1} = 0.0581 \log \frac{P}{1.9513 \times 0.205},$$

whence $P = 3.4 \times 10^{-10}$. This would mean that silver has a greater tendency to pass into the ionic condition in pyridine than in water, which would not be in harmony with the fact that the pyridine solutions do not conduct as well as the aqueous solutions. Again, although the dielectric constant of pyridine has apparently not been determined, it will, judging from analogy, very likely be found to be much lower than that of water.

Further attempts to calculate solution tensions will not be made, seeing that the requisite values of p are not available. It may be well, however, to call attention to one or two further cases in a general way. The difference of potential between — for instance — zinc and a solution of zinc chloride into which it dips varies from $+0.522$ volt, when the solvent is water, to -0.066 volt, when the solvent is quinoline. From this it is evident that the solution tension of the metal must diminish very greatly in the case mentioned. Silver behaves in the opposite way toward these solvents, its contact-potential toward the aque-

[1] Taken from No. 26.

ous solution being — 1.018 volt and toward the quinoline solution —0.617 volt. This would seemingly indicate that the solution tension of silver is greater toward quinoline than toward water.

The stupendous values that are found for the solution tensions of the metals toward water according to the formula given above are well known. The remarks recently made by R. A. Lehfeldt[1] concerning the extravagant figures deduced from measurements of E. M. F. appear to the author very timely indeed.

In order to ascertain how the E. M. F. of the chain, Ag| *n*/10 $AgNO_3$ in Pyridine| *n*/10$AgNO_3$ in Water|Ag varies, when in the first solution, water plus pyridine in various proportions is used as solvent instead of pure pyridine, the following determinations were made. The chain was the same as just given, both solutions remaining *n*/10 throughout. The solvent in the first solution was changed as indicated in the first column of the following table, while the second column gives the total E. M. F. The silver in the aqueous solution was the positive pole of the combinations throughout. The concentrations are given in parts of water by volume to one part of pyridine.

Conc. water	E. M. F. in volts	Conc. water	E. M. F. in volts
0	0.422	32	0.148
$\frac{1}{8}$	0.376	64	0.055
1	0.339	127	0.022
3	0.300	255	0.013
7	0.259	511	0.011
15	0.210		

From the table it appears that silver dipping into a silver nitrate solution in pyridine gradually becomes more positive toward the solution as the pyridine is replaced by water; but the potential changes less rapidly than proportional to the amount of water substituted.

If in the chain Ag|*n*/10$AgNO_3$ in Pyridine|*n*/10$AgNO_3$ in

[1] Zeit. phys. Chem. **26**, 94 (1898).

Water | Ag the concentration of the Ag ions in the pyridine solution be calculated according to the formula

$$\pi = \frac{RT}{e_o n_e} \log \frac{c_1}{c_2}$$

on the assumption that the solution tension of silver is the same toward pyridine as toward water, the result is that there are practically no silver ions in the pyridine solution, and that consequently the silver must be present in form of a complex ion. The fact that when ferric chloride and silver nitrate are brought together in pyridine solutions no precipitation results would seem to argue in favor of this view. But since silver chloride dissolves in pyridine and conducts, it may also be argued that silver ions and chlorine ions can exist side by side in pyridine (in a solvent be it remembered, that very likely has a lower dielectric constant than water) and that for this reason no precipitation occurs. It will not be contended that because aqueous solutions of ferric chloride and, for instance, copper nitrate do not give a precipitate of copper chloride no chlorine ions or copper ions are present and no copper chloride is formed. The explanation is simply that all the products formed are soluble. There is no reason to suppose that in a silver nitrate solution in pyridine the silver is present in form of a complex ion. The facts are, the molecular weight of the salt in pyridine is normal and the compounds that pyridine forms with silver nitrate are $(C_5H_5N)_2.AgNO_3$ and $(C_6H_5N)_3.AgNO_3$.[2] The latter compounds may be regarded as silver nitrate with two and three molecules of pyridine of crystallization just as truly as the compound $Cu(NO_3)_2.3H_2O$ is regarded as copper nitrate with three molecules of water of crystallization. No one maintains that when the latter compound is dissolved in water, copper is present in form of complex ions and there is no more reason for assuming that silver is present in form of complex ions in a pyridine solution of silver nitrate.

[1] Compare LeBlanc, Elektrochemie, 126.

[2] Compare Calm-Buchka. Chemie des Pyridins, 59.

The inference then is that the relatively higher E. M. F. of the chain last mentioned is due mainly to the high solution tension of the metal toward pyridine. But if this view be taken then in connection with the results of the last table, the conclusion follows that the solution tension of silver toward water increases as pyridine is added to the latter. If this in turn be admitted then it may be asked — why cannot the solution tension toward water be changed by dissolving in the latter any substance, solid, liquid or gaseous. It is to be borne in mind that thus far the electrolytic solution tension of a metal has always been considered constant (at a given temperature) toward aqueous solutions.

If the theory of the electrolytic solution tension be held at all, there seems no escape from the conclusion that the solution tension varies for different solvents and mixtures of solvents; and hence the dissolved substances — other than the simple ions of the metal in question — may exert an influence in determining the difference of potential between the metal and the solution. If the solution tension changes not only with the solvent but also with the dissolved substances present, it is questionable, to say the least, whether the hypothesis of an electrolytic solution tension is helpful at all. Certainly when the concentration of a certain kind of ion in a solution containing other substances also is to be found by the usual method of measurement of E. M. F. in the application of which the electrolytic solution tension is assumed to be constant, the fact that the latter assumption is a safe one to make must be proved in each case; how this can be done, is not easy to see.

Laboratory of Physical Chemistry, University of Wisconsin,
Madison, June 10, 1899.

NEW BOOKS

Traité élémentaire de Mécanique chimique, fondée sur la Thermodynamique. *By P. Duhem. Vol. III. 380 pp. Vol. IV. 381 pp. 18 × 25 cm. Paris. A. Hermann, 1898-99. Price: paper, each, 12 francs.* — The appearance of the present fourth volume of Duhem's *Traité* completes this monumental work on the theoretical aspect of physical chemistry. The first two volumes of the work have already been noticed in this journal (**1**, 426; **2**, 128); we have now to announce the appearance of the last two.

The introductory Vol. I. was devoted to an exposition of the principles of thermodynamics, in which the classical reversible thermodynamics is supplemented by Duhem's extension of the theory to what he terms 'false equilibria.' In the simple case of compression thermodynamics, to illustrate, the differential of the free energy ψ is

$$d\psi = -pdv - \eta dt;$$

whence $-p = \partial\psi/\partial v$ and

$$-dp = \frac{\partial^2\psi}{\partial v^2}\,dv + \frac{\partial^2\psi}{\partial v \partial t}\,dt. \qquad (1)$$

But for paths of false equilibria Duhem assumes that a function ψ always exists, as before, such that the energy is

$$\psi - t\frac{\partial\psi}{\partial t},$$

while (1) is replaced by

$$-dp = \frac{\partial^2\psi}{\partial v^2}\,dv + \frac{\partial^2\psi}{\partial v \partial t}dt + f(v, t, p)\,|\,dv\,|,$$

where f is a continuous function.

Detailed applications of thermodynamic theory begin in Vol. II., which contains the treatment of equilibria in one-component systems, and the theory of dissociation. Vol. III. considers homogeneous mixtures, and solutions, — the theory of solutions, in short. In the concluding Vol. IV., matters of detail are brought to a close by a study of 'double mixtures'. By double mixtures Duhem means two-component systems with two phases of variable composition. Under this head we find a formidable array of subjects: the theory of distillation, critical states of mixtures, liquefaction of mixed gases, two liquid layers, mixed liquids and their vapors, isomorphous mixtures, and so on. The volume is concluded by an extensive theoretical study of the phase rule, a pleasing

feature of which is the author's ample recognition of the bearing of variance upon the classification of chemical equilibria. It is unfortunate that the phase rule was not introduced earlier, and adopted as a guide in the classification of all the material in the work. A classification primarily according to the number of components and secondarily according to variance would have furnished an ideal arrangement of the matters in hand.

Duhem's book is peculiarly interesting in that it is the first attempt that has yet been made to present the theory of physical chemistry in a comprehensive way. Its method throughout is that of the energy theory: a mathematical description of the mutual transformations of work and the work-equivalents of the thermal and chemical effects that are producible by the expenditure of work. In its form and its matter it is the culmination of many years of special research.

With the exception of the topics of reaction velocities and electrochemistry, every branch of mathematical chemistry has received full consideration in it. The result is by no means a mere compilation of the work that has been done in the subject. Everything that is presented has been arranged in a definite scheme, and developed, in a most independent manner, by means of two of the thermodynamic potential functions, the free energy and the thermodynamic potential — the functions

$$\epsilon - t\eta$$
$$\epsilon - t\eta + pv,$$

in the notation of Gibbs.

The author's erudition is remarkable; and he has spared no pains to include the latest results of research, as many passages of his text bear witness. His style is everywhere clear, but those of us who love compact expression will think it somewhat diffuse. This is one reason why the book extends over fourteen hundred large pages. But, notwithstanding this fact, these volumes are very interesting reading; and for those who wish merely to gain a general view of their subject they will be far easier reading than would be the task of wading through the scattered and heterogeneous memoirs whose results they summarize from one same point of view. For the specialist, too, and as a reference manual for teachers, the work is a boon. No one, in fact, who is at all seriously interested in modern chemical theory can afford to be without it; and it should most certainly be on the shelves of every college library. It is provided with an index of authors cited, and with a list of the chemical substances whose thermodynamic behavior is discussed in the text.

J. E. Trevor

Geschichte der physikalischen Experimentierkunst. *By E. Gerland and F. Traumüller. 16 × 23 cm; pp. xvi and 442. · Leipzig: Wilhelm Engelmann, 1899. Price: paper, 14 marks; bound, 17 marks.* — The title of this book is somewhat too narrow. It is impossible in any real science to effect a complete separation of theory and practice, even when the science is in an advanced stage of development, and historically the two inevitably grow together, each depending on the other. The authors have therefore given a fuller account of the growth of physical theories than is implied by their title, and

the book is a much more interesting one than it would have been if the authors had limited themselves as strictly as their title indicates.

The work is divided into three parts: Part I., Antiquity (pp. 4–60), is devoted to the Babylonians and Assyrians, the Egyptians, and the Greeks and Romans. Part II., The Middle Ages (pp. 60–112), contains an account of the physical knowledge of the Byzantine Greeks, the Arabs and the West down to about the end of the sixteenth century. Part III., Modern Times (pp. 113-427), starts with Galileo and ends with the invention of the Morse telegraph and the Daniell cell. The plan of the work is thus seen to be quite comprehensive, and it should prove useful to teachers who believe in the advantages of the historical method, but who have not themselves the time or the opportunity to do all the necessary historical reading in the original works. The general reader in physics will also find the book interesting and the style as lively as can be expected.

The most important feature — aside from the copious references to the original sources which the authors have ransacked — consists in the very large collection of figures, which are, as far as possible, facsimile reproductions of the originals. It is curious to note the general and characteristic change in the forms of apparatus which came with the beginning of this century. The change is typical of the decay of prejudice in favor of the established order of things and of the awakening of the general common-sense, a change of which the French Revolution and the First Empire were the outward political signs. In the earlier times we find the apparatus and machines often more decorative than practical, and the figures and illustrations more artistic in composition and execution than clear and instructive. The demon of utilitarianism had not yet pointed out the folly of making life beautiful. In those earlier times scientific men were few: they belonged to the cream of a society where intellect and cultivation had not yet been separated, — Lionardo da Vinci was only the greatest of a class. But those golden days are gone. The real scientific men are almost as few as then, but there is a host of helpers each adding his mite to our sum of practical knowledge. This army of scientific laborers has grown to gigantic proportions, and though we are not Lionardos and have little time for anything that lies outside the range of our Ph.D.-examination or the particular subject we are hired to teach, we ought to be economical since we cannot be artistic. Our instruments nowadays are marvels of simplicity and neatness compared with the artistically cumbersome machines of a couple of centuries ago: but we have as yet gone only half way, and we have lost the beauty without carrying utility and economy to the bitter end. A vast majority of our scientific instruments are designed not only *by* but *for* the instrument maker, and there is a shocking lack of economy shown in the perpetuation of costly and antiquated details and in the irreproachable finish of surfaces and angles which double the price of our instruments without adding in the slightest degree to their accuracy or convenience. If instrument makers would profit by the example of American makers of machine tools, and would compare American tools with European, they would see that they are still in the antiquated European stage of development. And if physicists and all who have need of physical instruments would insist on proper design, the cost of fitting out a physical laboratory might be very greatly reduced.

To return to the volume before us: It is well printed and the figures are admirable; and, excepting a Teutonic dearth of margin, it is in all respects attractive in appearance. It is supplied with a table of contents and with author and subject indices, beside a list of the four hundred and twenty-four figures with the sources from which they have been taken.

The reviewer takes pleasure in recommending the work of Drs. Gerland and Traumüller to all who are interested in physics, and feels confident that they will find it both instructive and entertaining. *Edgar Buckingham*

Jahrbuch der Elektrochemie. *W. Nernst and W. Borchers. Vol. IV. 16 × 24 cm; pp. viii and 411. Halle: W. Knapp, 1898.* — As compared with preceding years scientific electrochemistry would appear to be developing faster than applied electrochemistry, one hundred and forty pages being allotted to the former and two hundred and forty to the latter as against seventy-two and two hundred and sixty in the preceding year. The review of the scientific development of the subject is almost exclusively the work of Danneel; Küster writing merely the chapter on electrochemical analysis. The technical development is outlined by Borchers, there being in addition a chapter on sources of current and one on organic synthesis, both by Elbs. *Wilder D. Bancroft*

Anwendungen der Infinitesimalrechnung. *By Arwed Fuhrmann. Theil I. Naturwissenschaftliche Anwendungen der Differentialrechnung. 14 × 23 cm; pp. xii and 148. Theil II. Naturwissenschaftliche Anwendungen der Integralrechnung. 14 × 23 cm; pp. xi and 268. Berlin: Ernst & Korn.*— The recent appearance of one of the six parts of Fuhrmann's 'Applications of the Infinitesimal Calculus' gives occasion to advert to the first two parts, 'Applications of the Differential Calculus', and 'Applications of the Integral Calculus', which of the entire series have the most interest for the physical chemist. Especial attention has been given in these volumes to the employment of the calculus in physicochemical problems; for which reason they can afford much help to the student who finds his reading hampered by a too meagre acquaintance with the customary mathematical methods. *J. E. Trevor*

Mathematical Essays and Recreations. *By Hermann Schubert. Translated, from the German, by Thomas J. McCormack. 16 × 24 cm; 149 pp. Chicago: The Open Court Publishing Co., 1898. Price: cloth 75 cents; paper 25 cents.* — The six mathematical essays assembled in the present volume treat in popular style a number of interesting mathematical topics. Number is regarded as the result of counting. It is shown that the different kinds of numbers, negative, fractional, irrational, imaginary, and complex numbers, are all obtained naturally and in order through application of the same simple principle, that all results of arithmetical operations are to be treated in the same way. This application of "monism" has made arithmetic a consistent system of logical forms. One of the essays elucidates the conservative and selfcontained character of mathematical knowledge. Another outlines the methods of formation of those wonderful arrangements of numbers, the magic squares. Another, on the fourth dimension, explains that n-dimensional totalities are those that require the specification of n numbers to indicate definitely any of their individuals.

Here is appended a vigorous refutation of the arguments for assuming an unseen world in a fourth dimension. Finally, and perhaps most interesting of all, is a delightfully written history of the squaring of the circle, from the earliest times down to the demonstration by Lindemann of the impossibility of the construction. Every essay in the collection is clear, sound, instructive, and entertaining. *J. E. Trevor*

Introduction to Algebra. *By G. Chrystal. 12 × 18 cm; pp. xviii and 412. New York: The Macmillan Co. (London: Adam and Charles Black), 1898. Price: cloth $1.25.* — Instead of beginning in the time-honored way, Professor Chrystal devotes the first fifty pages to the statement and elucidation of the fundamental laws of algebra. The application of these laws in simplifying algebraic expressions is then given, and the graphical representation of functions of a single variable is introduced. After which, equations of the first degree in one or more variables are carefully discussed, special attention being paid to the processes of derivation by means of which a given equation or set of equations may be replaced by an equivalent equation or set of equations. These first hundred and twenty pages from an excellent elementary algebra; the learner is not forced to wade through the uninteresting processes of division and of factorization, or the methods for determining the greatest common measure and the least common multiple, before getting to the really interesting and useful question of the solution of linear equations.

The remaining two-thirds of the book contain a thorough discussion of the properties of rational functions, and the usual discussions of irrationals, of ratio and proportion, of the progressions, of quadratic equations, and of permutations and combinations. The last chapter, of fifty pages, is a delightfully simple and clear graphical discussion of rational functions.

Not the least interesting feature of the book is the emphasis that the author lays upon the advantages of head work over finger work. For example (p. 362): "But we repeat our warning that, important as is dexterity of the fingers, he who cultivates this at the expense of accurate thought may become a successful worker of certain kinds of superficial examination problems, but a mathematician, or a successful applier of mathematics to things practical, never!" *Paul Saurel*

Scientia. *Exposé et Développement des questions scientifiques à l'ordre du jour. Recueil publié (pour la partie physico-mathematique) sous la direction de MM. Appell, Cornu, d'Arsonval, Friedel, Lippmann, Moissan, Poincairé, et Potier, Membres d l'Institut. Paris: Georges Carré et C. Naud. 1899. Price of each number, 2 francs. Subscription to a series of six numbers, 10 francs.* — Under the general title *Scientia*, the well-known publishing house of Carré and Naud has begun the issue of a series of short monographs on subjects of particular current scientific interest. These essays are primarily intended to aid the specialist in the task of keeping in touch with the newer developments of science that bear more or less directly upon his own special interests. Two series are under way, one for the mathematico-physical sciences, the other for the biological sciences. The names of the eminent men who are responsible for the conduction of the former of the two is a guarantee that its excellence will be what it should be.

The first number to appear is a volume on *La Théorie de Maxwell et les Oscillations Hertziennes*, by the famous analyst and physicist, H. Poincaré. This is an admirably arranged and most delightful little book of eighty pages (13 × 20 cm.). It will be of interest to everyone who is interested in the more impressive features of the progress of modern physics.

Further volumes in preparation are to treat Zeeman's phenomenon, stereochemistry, rare earths, the new gases, cathode rays, and so on. Messrs Carré and Naud have here undertaken an interesting and very useful enterprise.

J. E. Trevor

Neue gasometrische Methoden und Apparate. *By Otto Bleier. 16 × 24 cm; pp. x and 231. Vienna: Spielhagen & Schurich, 1898.* — Under this title the author presents in a clear and attractive manner his many modifications of well-known apparatus, together with a few forms distinctly his own. Most chemists are, doubtless, already familiar with the apparatus and methods now described, through the author's papers in the *Berichte der deutschen Gesellschaft*.

The volume is divided into five parts: The Measurement of Gases; II. Volumetric Gas Analysis; III. Gravimetric Gas Analysis; IV. Determination of Vapor-Tension; V. Calibration of Vessels, etc.

In each part the author devotes almost his entire attention to discussing the application of his own peculiar forms of apparatus to the various problems which arise in the measurement and analysis of gases, so that in reality the book has not the comprehensive character the part headings would lead one to expect. The work is not intended as a manual of gas analysis.

The chief value of the volume lies in its usefulness in suggesting to investigators various convenient forms of apparatus for special or unusual conditions, rather than as a reference book for the gas analyst. Any discussion of the apparatus or methods described is impossible without the accompanying figures. The interested reader is, therefore, referred to the volume itself or to the original papers in the *Berichte*.

The illustrations accompanying the text are clear, neat, and well printed, though sufficient care was not exercised in a few cases to maintain relative proportions of the different parts. The general make-up of the book is excellent, the typography is admirable, the text is quite free from errors, and, with its wide margins and heavy paper, the volume attracts one at once.

Up to the present time Bleier's work is the only one which has devoted so much space to the consideration of exact gas measurement, and which has attempted to bring together so many different forms of modern gas analytical apparatus. Had the author been satisfied with this, and with an explanation of the special value of each form, he would have filled a long-felt want. It is greatly to be regretted that he has, instead, devoted so much space to showing in how many different ways the older forms of apparatus can be modified. Thus, while one cannot fail to be struck with his ingenuity in devising all sorts of changes, one is apt to question whether genuine improvements have been the result. The volume is, however, replete with suggestions, and therefore a welcome addition to the reference shelf of the library. *E. M. Chamot*

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry

General

The atomic weight of tellurium. *R. Metzner. Comptes rendus*, **126**, *1716 (1898)*. — The author has determined the amount of tellurium in tellurium sulfate and in tellurous acid. The final value is 127.9. *W. D. B.*

On the atomic weight of tellurium and its bearing on the multiple proportions of the atomic weights of the other elements. *H. Wilde. Comptes rendus*, **127**, *613 (1898)*. — The value of 127.9 for tellurium obtained by Metzner (preceding review) approaches very closely the value of 128 adopted by Dumas for theoretical reasons. The author reasserts his belief that the law of the triads is more exact then the experimental data. *W. D. B.*

On the positions of tellurium and iodin in the periodic system of the elements. *H. Wilde. Comptes rendus*, **127**, *616 (1898)*. — Tellurium and iodin do not fit into the periodic system and it is claimed that the positions of boron, gold, mercury, lead and other elements are anomalous. The author makes the point that Mendeleef's famous predictions were really based on Dumas's classification by families and not on the periodic system at all. *W. D. B.*

On the atomic weight of nitrogen. *M. Vèzes. Comptes rendus*, **126**, *1714 (1898)*. — From a study of the physical properties of nitrogen, Leduc and D. Berthelot each decided that the atomic weight of nitrogen should be 14.005. Stas found 14.044 by chemical methods and this discrepancy was attributed by Leduc and D. Berthelot to the fact that the value of Stas for silver was not right owing to occluded oxygen. It is pointed by the author that Stas made one series of measurements to determine the amount of this error and that his corrected value for nitrogen was still 14.040. *W. D. B.*

On the molecular weights of easily liquefiable gases. *D. Berthelot. Comptes rendus*, **126**, *1415, 1501 (1898)*. — Taking the densities and the variations from the gas law as a basis (**3**, 174) the author calculates the atomic weights of carbon, nitrogen, chlorin, and sulfur from the data for carbonic acid, acetylene, N_2O, hydrochloric acid, and sulfur dioxid. The values decided upon are O 16, H 1.0074, C 12.005, 14.005, S 32.046, Cl 35.479, and argon 39.882. The value for argon is obtained from the density and the critical data. *W. D. B.*

New gases in the atmospheric air. *W. Ramsay and M. W. Travers. Comptes rendus,* **126,** *1610, 1761 (1898).* — Reviewed (**3,** 174) from Zeit. phys. Chem. **27,** 564 (1898).

Spectrum investigations of atmospheric air. *H. Moissan and H. Deslandres. Comptes rendus,* **126,** *1689 (1898).* — This is a sealed paper deposited early in 1896 in which the authors record that a study of the spectrum of the gas evolved from cerite points to the existence of hitherto unknown elements. The sealed paper was opened at this time owing to Ramsay's discovery of krypton. *W. D. B.*

On a new radio-active substance contained in pitchblende. *P. Curie and S. Curie. Comptes rendus,* **127,** *175 (1898).* — It had already been found by Mme. Curie (**3,** 190) that natural chalcolite was much more active in emitting Becquerel rays than the artificial mineral and the opinion was expressed that this discrepancy was probably due to the presence of an unknown element. Attempts have since been made to isolate this element from pitchblende. While this has not yet been accomplished the authors have obtained a substance which should be bismuth sulfid but which is about four hundred times as active as uranium. It seems probable therefore that the new element, to which the name of polonium is to be given, is akin to bismuth. *W. D. B.*

On a new markedly radio-active substance in pitchblende. *P. Curie, S. Curie and G. Bémont. Comptes rendus,* **127,** *1215 (1898).* — In addition to the bismuth sulfid which contained polonium, the authors have obtained a salt which is apparently barium chlorid but which is nine hundred times as active as uranium. The spectrum of this salt shows a line that has not yet been attributed to any known element. This line becomes more intense as the radio-activity increases. It is proposed to call the new element radium. *W. D. B.*

New method of determining the mechanical equivalent of heat. *J. B. Baille and C. Féry. Comptes rendus,* **126,** *1494 (1898).* — The authors measure the rise of temperature in a copper cylinder when the alternating current from a small dynamo is passed around it. This communication is merely a preliminary one and deals chiefly with the correction for loss of heat by radiation.

W. D. B.

Regnault's calorie and our knowledge of the specific volumes of steam. *G. P. Starkweather. Am. Jour. Sci. (4)* **7,** *13 (1899).* — This is a careful digest of the work that has been done on the specific and latent heat of water with application to the determination of the specific volumes of steam. The author discusses what he terms Regnault's calorie and endeavors to show that the statement made by Regnault, some twenty years after his experiments, that his determinations were in terms with the air thermometer, are justified by the results themselves. A summary of the results of the mean specific heat between 0°–100° for different observers show that the variations are about equal above and below Regnault's. Taking $C_{0\text{-}100}$ as equal to 1.00358C (Regnault's value) then the more reliable determinations deviate from this

Rowland (mixtures)	+0.0005
Ludin "	+0.0018
Dieterici (Mech. Equiv.)	+0.0044
Reynolds "	—0.0050

The larger part of the paper is devoted to a discussion of the total heat of steam and a complete study of Regnault's results. It all points to a very strong substantiation of Regnault's work within certain limits included in the saturation line, but shows that for superheated steam all previous results are much too discrepant to be utilized. *H. T. B.*

On the avoidance of the error in the Andrews method of estimating the specific heat of a liquid. *L. Pfaundler. Wied. Ann.* **67,** *439* (*1899*). — As was to be expected the author, who has done so much towards perfecting the Andrews method of measuring specific heats, shows in the present paper that, by a proper construction of the apparatus and by rational experimental precautions, the error pointed out by Gumlich and Wiebe (**3,** 170) may be very simply avoided. *H. T. B.*

On an apparatus for measuring very high pressures. *A. deF. Palmer, Jr. Am. Jour. Sci.* (*4*) **6,** *451* (*1898*). — From results obtained for the change of the electrical resistance of mercury with pressure the author makes use of his formula deduced in order to extrapolate in finding higher pressures, and designs an apparatus for testing the limit of pressure obtained with a tinned screw. A Bessemer steel screw broke at 3554 atmospheres, while a carefully annealed stubb steel screw began to twist at 3600 atm. and broke at 4385. The author gives a plot showing how the volume change of the substance under compression changes with the turns of the screw. *H. T. B.*

On an improvement to a standard barometer. *F. R. Koch. Wied. Ann.* **67,** *485* (*1899*). — In 1895 the author described a new form of barometer that he had designed with a view to its being adopted in place of the so-called standard barometers. Amongst the new features was the filling of the barometer tube by distillation during the time it was being exhausted by a mercury pump, the introduction of a pair of thermometers in the mercury column itself and the use of an attached Geissler tube to determine the state of the vacuum over the mercury column. Between the barometer with its attached tubes, and the mercury pump was placed a large mercury trap. The improvement now brought out is the introduction, in place of the mercury trap, of a Sprengel pump to be a part of the complete apparatus. *H. T. B.*

On a new form of volumenometer. *A. Oberbeck. Wied. Ann.* **67,** *209* (*1899*). — The author modifies Paalzow's apparatus for estimating the specific gravity of solids. His method is a difference one and as such is independent of the barometer. Two bulbs, in one of which is placed the substance whose specific gravity is to be determined are connected to two narrow-bore tubes meeting in a Y and connecting with a mercury reservoir. On opening the bulbs, the mercury is allowed to run up the glass tubes to a fixed mark. The bulbs are then closed and the mercury reservoir lowered. The readings of the mercury threads with the two bulbs empty and when the solid is placed in one of them give the volume of the solid from the diminution in pressure.

H. T. B.

One-Component Systems

Reply to a claim of priority by M. Marqfoy. *D. Berthelot. Comptes rendus*, **126**, *1262* (*1898*). — The point made is that it is merely a definition to state that "the molecular weight of a gas is proportional to the product of its density into its molecular volume". *W. D. B.*

Melting-points of some substances under high pressures. *E. Mack. Comptes rendus*, **127**, *361* (*1898*). — Measurements have been made with naphthalene, napthylamin, diphenylamin and *p*-toluidin. No sign of a maximum freezing-point could be detected. The freezing-point of naphthalene was raised to 150.6° by a pressure of 2140 atm. *W. D. B.*

On the boiling-point of liquid ozone. *L. Troost. Comptes rendus*, **126**, *1731* (*1898*). — The ozone was formed at −79° and then liquefied. It boiled under atmospheric pressure at −119°. The value obtained by Olszewski was −106°. *W. D. B.*

On the liquefaction of hydrogen and helium. *J. Dewar. Comptes rendus*, **126**, *1408* (*1898*). — Reviewed (**2**, 505) from Jour. Chem. Soc. **73**, 528 (1898).

Preparation of crystallized calcium. *H. Moissan. Comptes rendus*, **126**, *1753* (*1898*). — The previous methods for obtaining calcium are reviewed briefly. Pure calcium may be obtained crystalline by crystallization from liquid sodium at red heat or by electrolysis of fused calcium iodid. In the first method calcium iodid is added to an excess of liquid sodium; after cooling, the sodium is removed with alcohol. About forty grams of pure calcium have been obtained in one operation by this method. *W. D. B.*

Properties of calcium. *H. Moissan. Comptes rendus*, **127**, *584* (*1898*). — Pure calcium scratches lead, but not calcium carbonate; it melts at 760° and its density is 1.85; in color it resembles silver. It is not attacked by chlorin, bromin or iodin in the cold. It starts to burn in oxygen at 300° and the heat evolved is so great as to volatilize some of the lime formed. When heated in the air the metal takes up oxygen and nitrogen. Calcium combines readily with phosphorus and with lamp-black, not so readily with sulfur. It forms crystalline alloys with magnesium, zinc, tin and mercury but not with sodium and potassium. *W. D. B.*

The color of calcium carbid. *H. Moissan. Comptes rendus*, **127**, *917* (*1898*). — Pure calcium carbid is colorless and transparent. *W. D. B.*

The properties of aluminum. *A. Ditte. Comptes rendus*, **127**, *919* (*1898*). — Aluminum is not attacked after the first few minutes by any dilute acid except hydrochloric acid owing, as the author says, to the formation of a thin film of hydrogen on the surface. It is not attacked permanently by sodium chlorid owing to the formation of alumina. The metal is attacked by a mixture of sodium chlorid and acetic acid. *W. D. B.*

On the specific heat of air at constant pressure. *A. Leduc. Comptes rendus*, **126**, *1860* (*1898*). — It is claimed that Regnault's own experiments show the specific heat of air at constant pressure to be 0.239 and not 0.2375. *W. D. B.*

On the ratio of the two specific heats of gases and its variation with the temperature. *A. Leduc. Comptes rendus*, **127**, *659* (*1898*). — For air the ratio of the specific heats apparently does not vary between zero and one hundred degrees. With carbonic acid the ratio decreases with rising temperature. Taking this into account the author proposes to show that the ratio at 0° for a perfect diatomic gas is 1.4; for a perfect triatomic gas 1.267. Following out the line of reasoning, the author concludes that the value 1.66 might be obtained with a diatomic gas as far removed from the state of an ideal gas as is sulfur dioxid at 10° under the atmospheric pressure. *W. D. B.*

On the ratio of the two specific heats of gases. *L. Boltzmann. Comptes rendus*, **127**, *1009* (*1898*). — While admitting the possibility of Leduc's hypothesis (preceding review) that mercury vapor may not be monatomic even though the ratio of the specific heats is 1.66, the author inclines to the belief that this agreement between the theoretical value for a monatomic gas and that obtained experimentally by Kundt and Warburg is not a mere coincidence. *W. D. B.*

Two-Component Systems

The accurate determinations of freezing-points and some applications to aqueous solutions. *F. M. Raoult. Zeit. phys. Chem.* **27**, *617* (*1898*). — The most serious source of error in the thermometer is the displacement of the zero, a change which is, of course, accelerated by jarring. The author keeps his thermometer always vertical and surrounds it with melting ice when not in use. With a thermometer having five centimeters to the degree a change of one millimeter in the barometric pressure means a difference of 0.0002° in the reading. The thermometer should always be read with a telescope. The author keeps the temperature of the freezing bath constant by passing a regulated current of air through the ether with which the bath is filled. About one liter of ether is used up every ten hours. The freezing-vessel itself is protected at the top by discs of cloth. The solution is stirred by a vertical screw run by a turbine. The outside bath is kept 0.1° below the freezing-point of the water or of the solution at the time that ice separates, but the water or the solution is supercooled 0.5° before a crystal is added. It is important that the freezing-point of pure water should be determined before and after that of the solution.

The influence of the temperature of the bath is to be eliminated by making the convergence temperature coincide with the observed freezing-point. It was found in determining the convergence temperature that the difference between this and the temperature of the freezing-bath depends chiefly on the rate at which the stirrer revolves. If an ice mantle forms on the walls of the freezing-vessel the apparent freezing-point will be too high instead of too low. To eliminate the effect of supercooling, three observations are made with three different amounts of supercooling and the value for zero supercooling obtained from these by extrapolation.

Experiments with dissolved oxygen gave 22.1 for the molecular lowering of the freezing-point instead of the theoretical 18.5; but this discrepancy the author thinks is to be attributed to experimental error, since the maximum accuracy to be obtained in cryoscopic measurements is estimated to be $\pm$ 0.0002°.

The following molecular lowerings were obtained in dilute solutions : sugar 18.7, alcohol 18.3, sodium chlorid 37.2, potassium chlorid 36.8. Alcohol seems to show a slightly decreasing molecular lowering as the solution becomes very dilute. The author's data for the four substances agree well with those of Loomis, Nernst and Abegg, and Wildermann ; but not with those of Ponsot. Reasons are given for believing that Ponsot's measurements are not very accurate, the error being chiefly in the method of stirring. *W. D. B.*

Cryoscopic investigations in the terpene series. *W. Biltz. Zeit. phys. Chem.* **27,** *529* (*1898*). — Cryoscopic determinations of benzene solutions of fenchone, menthone, tanacetone, isothujone, pulegone, carvone, carvenone, dihydrocarvone, citronellal, citral, cineol, pinol, citronellyl alcohol, geraniol, menthol, dihydrocarveol, *l*-borneol, linalool, terpineol, carvacrol, thymol, isoborneol, fenchyl alcohol ; also the naphthalene solutions of *cis*-terpin and *trans*-terpin. The substances containing no hydroxyl group, such as fenchone, menthone, tanacetone, isothujone, pulegone, carvone, dihydrocarvone, citronellal and citral give apparent molecular weights varying but little with the concentration. Carvenone shows the same typical curve and is therefore a ketone. All the alcohols show increasing molecular weight with increasing concentration, the variation being most marked with the primary alcohols and least so with the tertiary alcohols. Borneol and isoborneol give markedly different curves, the first being that of a secondary alcohol, the second that of a tertiary alcohol. The author declines however to draw the conclusion that isoborneol is a tertiary alcohol. *W. D. B.*

The ammoniacal silver bromids. *R. Jarry. Comptes rendus,* **126,** *1138* (*1898*). — The author has determined the dissociation pressures at different temperatures of $AgBr3NH_3$ and of $AgBr1.5NH_3$; also the solubility curve at 0°. Addition of ammonia causes increased solubility of silver bromid while this salt or AgBr 1.5 NH_3 is solid phase. When $AgBr3NH_3$ is solid phase increasing concentration of ammonia means decreasing concentration of silver bromid. *W. D. B.*

On the compounds of lithium chlorid with ammonia and with methylamin. *J. Bonnefoi. Comptes rendus,* **127,** *367, 516* (*1898*). — Measurements of the dissociation pressures of the compounds $LiCl4NH_3$, $LiCl3NH_3$, $LiCl2NH_3$ and $LiClNH_3$ at different temperatures. From these data the author has calculated the heats of dissociation which agree satisfactorily with the values obtained by direct measurement. Corresponding data were obtained for lithium chlorid and methylamin except that the compound with four of methylamin could not be obtained. *W. D. B.*

New compounds of phenylhydrazin with certain metallic salts. *Pastureau. Comptes rendus,* **127,** *485* (*1898*). — Bismuth chlorid and nitrate can each crystallize with six of phenylhydrazin ; manganese and zinc sulfites each with two of phenylhydrazin. *W. D. B.*

Absorption of liquids by textile stuffs. *L. Vignon. Comptes rendus,* **127,** *73* (*1898*). — It was found that the ratio of liquid absorbed to weight of substance was constant to within one percent for each liquid and each textile stuff.

The order of absorption with all liquids is silk, wool, cotton, the cotton being the least absorbent. The amount of liquid absorbed varied with the nature of the liquid, the order being glycerol, olive oil, nitrobenzene, anilin, alcohol, benzene and water, this last being the least absorbed. The phenomenon is certainly connected with the extent of surface presented by the textile stuffs; but it is not possible to say whether this is the only factor or not. *W. D. B.*

Preparation of lithium ammonium, calcium ammonium and the amids of lithium and calcium. *H. Moissan. Comptes rendus*, **127**, *685 (1898).* — The compound of lithium and ammonia has the formula $LiNH_3$; that of calcium and ammonia the formula $Ca(NH_3)_4$. The author likes to consider these substances as substituted ammonium compounds though he offers no satisfactory reason for this. The lithium and calcium compounds, besides losing ammonia, dissociate to a certain extent forming hydrogen and amid $LiNH_2$ or $Ca(NH_2)_2$. *W. D. B.*

On calcium amalgam. *J. Ferée. Comptes rendus*, **127**, *618 (1898).* — By distilling under 12 mm pressure about one kilogram of liquid calcium amalgam, the author obtained twelve grams of a solid amalgam having apparently the composition Ca_3Hg_4. There is however no evidence to prove that this substance is really a compound. On heating the amalgam in a current of nitrogen, the nitride Ca_3N_2 was obtained. *W. D. B.*

On the compressibility of air when considered as a mixture of gases. *E. H. Amagat. Comptes rendus*, **127**, *88 (1898).* — The author points out that from a study of his own experiments he had deduced, in 1880, the following conclusion: "In the air the oxygen and nitrogen appear to be compressed separately as if they were alone under the total pressure of the mixture and not as if under the partial pressure which they exert in the mixture." This is identical with the law recently enunciated by Leduc (**3**, 179). *W. D. B.*

On mixtures of gases. *D. Berthelot. Comptes rendus*, **126**, *1703 (1898).* — The author proposes a formula of the van der Waals type for a mixture of two gases and shows how the constants A and B for the mixture can be calculated from the corresponding constants for the single gases. *W. D. B.*

On mixtures of gases. *J. D. van der Waals. Comptes rendus*, **126**, *1856 (1898).* — The author points out that he himself has applied his formula to mixtures of gases. He doubts however whether it is possible to calculate the constants of the equation from the constants of the single gases, as has been attempted by D. Berthelot (preceding review). *W. D. B.*

On mixtures of gases. *A. Leduc. Comptes rendus*, **126**, *1859 (1898).* — The author claims that D. Berthelot (two reviews back) should take into account the atomicity and molecular mass of each gas as well as the critical data. *W. D. B.*

The aqueous solutions of the soaps. *L. Kahlenberg and O. Schreiner. Zeit. phys. Chem.* **27**, *552 (1898).* — It was found that concentrated soap solutions have no true boiling-point, the whole mass of the solution foaming up into soap-bubbles. For this reason molecular weight determinations cannot be

made in this way. Some determinations made by the cryoscopic method with sodium oleate gave values corresponding to double the formula weight.

The soaps are good conductors of electricity and therefore not to be classed as colloids. The conductivity determinations showed that there is a good deal of hydrolysis in soap solutions. *W. D. B.*

The thermodynamic relations of hydrated glass. *C. Barus. Am. Jour. Sci.* (*4*) **7**, 1 (*1899*). — The author notes briefly further results obtained from a study of fusible water-glass. The reaction of hot water on glass at 200° shows at first volume-contraction and increase of compressibility, and then a second stage is manifest when the volume-contraction falls off to zero, and the compressibility, after passing through a maximum, diminishes rapidly. On cooling, bubbles appear in the clear water-glass showing that solidification takes place centrifugally. The glass is at first hard, but finally disintegrates and becomes a crumbling mass. From a thermodynamic point of view the author regards this as "a march through the critical region of certain phases of the water-glass examined". He considers two principal phases. Phase I, stable during the first part of the reaction, with dilute water-glass. Phase II, stable at the end of the reaction, with the concentrated water-glass and subsidence of volume-contraction. At the middle of the reaction Phases I and II are stable in presence of each other. He considers that both stages correspond to steep isotherms. *H. T. B.*

The compressibility of colloids, with application to the jelly theory of the ether. *C. Barus. Am. Jour. Sci.* (*4*) **6**, *285* (*1898*). — The first part of the paper is devoted to a study of the compressibility of water, colloidal solutions of gelatine and albumen in water and in ethereal solutions of caoutchouc. The solution is drawn into a long fine-bore tube, about 0.3 mm and held in the central part by two columns of mercury above and below. The pressure is applied through the lower column. The results show that the compressibility is essentially determined by the solvent for a wide range of concentration and through enormous variations of viscosity so long as the solution is liquid. The second part of the paper is a study of the coagulated liquid colloid, that is when it changes from a viscous liquid to a soft solid. Using the same tubes as in the former case, the author finds that when the pressure becomes great and is gradually increased the centre of the mercury column rises conoidal, becoming more and more sharply defined until a fine globule of mercury about 0.1 mm in diameter is projected upwards through the jelly-like mass of colloid. Sometimes a number of these globules are shot up. The speed and character of the drops evidently depend on the nature of the surface. The author recognizes that there is a vast difference between the viscous liquid solution and the coagulated colloid. Two states are however manifest in the latter case which throw some light on the idea of a jelly-like ether: the condition of non-compressibility as a solid, and the effect produced by the projection of these fine globules of mercury through the mass when the pressure becomes great enough to produce axial rupture. This causes a break-down in the solid state in the path of the projectile along which, before the solid has had time to heal, the pressure is transmitted hydrostatically. The idea of the phenomenon of spark discharge and movements in the ether generally are discussed at some length. *H. T. B.*

Poly-component Systems

Equilibrium in the system: water, ammonium chlorid, ferric chlorid. *E. C. J. Mohr. Zeit. phys. Chem.* **27,** *193 (1898).*— From aqueous solutions of ferric chlorid plus ammonium chlorid, crystals form that contain both these salts. These crystals had been investigated by Retgers, Schroeder van der Kolk and Roozeboom. As the first two investigators did not agree in their views as to the nature of these crystals the author investigated the equilibrium relations of the system at the suggestion of Roozeboom. Solubility determinations were made at 15°, 25°, 35°, and 45°. The solid phases that may exist in presence of the solution are hydrated ferric chlorid, the double salt of Fritsche ($FeCl_3.2NH_4Cl.H_2O$), mixed crystals of ammonium chlorid and ferric chlorid varying from 7 % to 0 % in their content of the latter salt. Along the boundary curve with hydrated ferric chlorid and double salt as solid phases, the amount of ammonium chlorid contained in the solution does not vary with change of temperature; the same is true of the ferric chlorid content of the solution along the boundary curve with double salt and mixed crystals as solid phases. This causes a probable intersection of these boundary curves at approximately — 15°, at which temperature the curve of the double salt would disappear. Two new double salts were found — $FeCl_3.NH_4Cl$ and $2FeCl_3.NH_4Cl.4H_2O$. The latter crystallizes in the regular system and was formerly regarded as a regular hydrate of ferric chlorid. This salt forms in solutions containing but small amounts of ammonium chlorid. The former double salt crystallizes in needles that are probably rhombic. No definite conclusions are reached concerning the nature of the mixed crystals. The author thinks they are mixtures of $FeCl_3.2NH_4Cl.H_2O$ with NH_4Cl. *L. K.*

The states of equilibrium in the ternary system: lead, tin, bismuth. *G. Charpy. Comptes rendus,* **126,** *1569 (1898).* — The author has determined the freezing-points of mixtures of lead, tin and bismuth. The results are plotted in a triangular diagram and discussed from the point of view of the phase rule. The temperature of the quintuple point is 96°. *W. D. B.*

The solubility of acids in solutions of the salts of other acids. *A. A. Noyes and E. S. Chapin. Jour. Am. Chem. Soc.* **20,** *751; Zeit. phys. Chem.* **27,** *442 (1898).* — The solubility (at 25°) of benzoic acid is investigated in solutions of sodium acetate containing 0.01321, 0.02641, and 0.05282 g-mol. per liter, also in sodium formate solutions containing 0.01414, 0.02828, and 0.05657 g-mol. per liter. The results are compared with those calculated according to a formula by Noyes (Zeit. phys. Chem. **27,** 275). In the case of the acetate solutions the found values exceed the calculated by 0 82 %, 1.19 % and 1.51 % respectively; in the case of the formate solutions the results deviate from the calculated by + 0.96 %, + 0.77 %, and — 0.50 % respectively.

As but three experiments were made in each case in which the ranges of concentration are not great, and as the deviations increase regularly in the one, and decrease regularly in the other series, the results can hardly be considered a noteworthy confirmation of the theory of electrolytic dissociation and the law of the influence on solubility as the authors claim. *L. K.*

Action of hydrogen on silver sulfid and the reverse reaction. *H. Pélabon. Comptes rendus*, **126**, *1864* (*1898*). — Above 350° the same equilibrium is reached whether one starts from hydrogen and silver sulfid or from hydrogen sulfid and silver. With rising temperature the ratio of hydrogen to hydrogen sulfid at equilibrium increases. Between 250° and 350° different states of equilibrium are reached when starting from the two ends. Below 250° apparently no reaction takes place. *W. D. B.*

Displacement of metals by hydrogen. *A. Colson. Comptes rendus*, **127**, *961* (*1898*). — Metallic silver is precipitated from Ag_3PO_4 by dry hydrogen. Raising the temperature or increasing the pressure increases the reaction velocity. At low temperature the metallic silver is black; at higher temperature white. *W. D. B.*

On the zones of reactions. *A. Colson. Comptes rendus*, **126**, *1505* (*1898*). — An application of the volume-temperature diagram to the case of dissociation. It is pointed out that the line for no decomposition and for complete decomposition may coalesce at some point just as the dew-line and the boiling-line are part of one and the same curve. *W. D. B.*

The boiling-points of mixed solutions. I. *T. W. Richards and W. L. Harrington.* **II.** *C. M. C. Gordon, L. J. Henderson, and W. L. Harrington. Zeit. phys. Chem.* **27**, *421*, *425* (*1898*). — One gram-molecule of cadmium oxalate in ten liters of water containing a slight excess of hydrochloric acid gives a depression of the boiling-point of 0.101°. The explanation given is that cadmium chlorid and oxalic acid, two compounds that are but slightly dissociated especially in the presence of hydrochloric acid, are formed. On the assumption that these products are undissociated and that normal hydrochloric acid is 0.8 dissociated the calculated depression of the boiling-point is 0.083°. Taking the actually observed values of the boiling-points of solutions of oxalic acid, hydrochloric acid and cadmium chlorid, the calculated depression becomes 0.093. The authors incline to ascribe the fact that the observed value is so high to the formation of molecular compounds. Similar results were obtained with cadmium citrate in hydrochloric acid solutions. The calculated depression of the boiling-point was 0.364° and the found 0.434° in this case.

Calcium sulfate was dissolved in sodium chlorid solution and the depression of the boiling-point was noted. Cadmium chlorid and sodium sulfate form in the solution and these are less dissociated than the original salts. Even if cadmium chlorid and sodium sulfate are considered as undissociated, the calculated depressions 0.081 and 0.036 are considerably less than the observed 0.093 and 0.060 respectively in the cases investigated.

The authors very appropriately remark that the results obtained clearly present additional evidence that the degree of dissociation as determined by the conductivity method and as deduced from the law of mass action do not agree. They arrive at the conclusion that either the degree of dissociation of sodium chlorid as determined from the conductivity is wrong or polymerization or formation of a double salt occurs even when the amount of cadmium sulfate is very small. *L. K.*

On the selenate of copper and its use in the preparation of selenic acid. *R. Metzner. Comptes rendus*, **127**, *54* (*1898*). — Selenous acid is oxidized by chlorin and the solution neutralized with cupric oxid. Owing to the great solubility of cupric chlorid, practically the whole of the cupric selenate can be obtained pure before the two salts begin to separate simultaneously. The copper selenate is converted into selenic acid by electrolysis, care being taken to avoid reduction of the selenic acid. The solubility of copper selenate was determined at 15°, 35° and 55°. At about 70° a basic salt precipitates.

W. D. B.

On some halid salts of lead. *V. Thomas. Comptes rendus*, **126**, *1349* (*1898*). — The author doubts the accuracy of Herty's statement that lead chlorid and iodid form solid solutions. In this paper it is stated point-blank that PbClI is a definite compound; but no adequate reasons are forthcoming.

W. D. B.

Action of acetylene on the metal ammoniums. *H. Moissan. Comptes rendus*, **127**, *911* (*1898*). — Sodium, potassium, lithium and calcium ammoniums react with acetylene forming monosubstituted acetylids, ethylene and ammonia.

W. D. B.

Action of ammonium persulfate on the silver of a photographic negative. *Lumière Bros. and Seyewetz. Comptes rendus*, **126**, *1639* (*1898*). — Ammonium persulfate can be used for improving an over-dense negative because it has the curious property of dissolving silver from the thickest portions of the negative. The authors account for this by assuming two reactions, a formation of a silver ammonium sulfate by the action of the ammonium persulfate on metallic silver and a reduction of the silver salt to silver with evolution of oxygen by the ammonium persulfate. The first reaction takes place nearest the glass where the concentration of the ammonium persulfate is the lowest and the second at the surface of the negative. The explanation is not entirely satisfactory; but the process is said to be a good one. A five percent solution of ammonium persulfate is said to be the best to use. *W. D. B.*

Action of ferric chlorid on aromatic compounds. *V. Thomas. Comptes rendus*, **126**, *1211* (*1898*). — If boiling benzene be treated with ferric chlorid there are formed different chlorin substitution-products running up to hexachlorbenzene. The reaction appears to be general and tetrachlortoluene has been prepared in this way from toluene. *W. D. B.*

Interchange of halogens in the aromatic series. *V. Thomas. Comptes rendus*, **127**, *184* (*1898*). — Ferric chlorid acts on *p*-dibrombenzene forming pentachlorbrombenzene. *W. D. B.*

Volumetric analysis of a mixture of phosphoric acid and its esters. *J. Cavalier. Comptes rendus*, **126**, *1142*, *1214*, *1285*; **127**, *60* (*1898*). — It has been known that phosphoric acid acted like a monobasic acid with methyl orange and like a dibasic acid with phenolphthalein. It has now been found that the mono-ester behaves in exactly the same way while the di-ester acts as a monobasic acid both with methyl orange and with phenolphthalein. On titra-

ting a mixture of these three acids with barium hydroxid using methyl orange as an indicator we find the total phosphates present. Continuing the titration with phenolphthalein as indicator we find the total amount of phosphoric acid and mono-ester. The insoluble salt $BaHPO_4$ is separated from the solution, dissolved in a known amount of hydrochloric acid and the solution titrated with methyl orange as indicator. The author has also determined the heats of neutralization of the different acids. *W. D. B.*

Volumetric analysis in alkaline solution with a ferrous salt. *A. Job. Comptes rendus*, **127**, *59* (*1898*). — Sodium pyrophosphate and a ferrous salt give a colorless solution eminently suitable for volumetric analysis. From qualitative experiments it appears that this solution is a more powerful reducing agent than stannous chlorid. *W. D. B.*

Osmotic Pressure and Diffusion

The relation between osmotic work and osmotic pressure. *Arthur A. Noyes. Zeit. phys. Chem.* **28**, *220* (*1899*). — In a previous article, Ibid. **23**, 60, the author made use of a circular process to determine the relation between osmotic pressure and work in a way somewhat different from that of other investigators. Dieterici wrote objecting to certain criticisms and Noyes avails himself of the opportunity to explain his position again. The gist of Noyes' contention is that it is not correct to assume that a finite quantity of a solvent can be removed from a solution without altering the concentration of the latter. A process should be considered in which solvent is added at the same time and in the same measure in which it is removed. Results of this method of calculation differ from Dieterici's by two per cent or less for moderately dilute solutions. For more concentrated solutions the difference rises to 3.38 %. *S. L. B.*

The meaning of osmotic pressure in the thermodynamics of solution. *N. Schiller. Wied. Ann.* **67**, *291* (*1899*). — This is a purely mathematical discussion of solution pressures and heats of dilution from the standpoint of thermodynamics. The treatment is clear though rather too extended, as such papers are apt to be. The author takes up first of all the question of the change in vapor-tension by pressure on the surface of separation. Kirchhoff's law for the heat of dilution of solutions is discussed and exception taken to the expression representing the disturbing action of concentration or dilution on account of the neglect of the specific volume of the added solvent in comparison to that of the vapor. The author proceeds to deduce what he terms a better expression for the heat of dilution and concludes by discussing at length the question of the heat of solution of absorbed gases. *H. T. B.*

Experimental contribution to the theory of osmotic pressure. *K. Schreber. Zeit. phys. Chem.* **28**, *79* (*1899*). — The question treated is whether the kinetic theory of gases can be directly applied to solutions. A gas exerts a pressure according to the equation $pv = RT$, and besides this it may exert a wind pressure, as for example the winds in the atmosphere. An electric stream passing through an electrolyte sets up winds of the ions. If a membrane permeable to the solvent and one ion is inserted in the solution, it will sustain a pressure in excess of the osmotic pressure analogous to that caused by a wind. Pfeffer cells

were used and a copper ferrocyanid membrane. This is permeable to water and NO_3 ions but not to Cu ions. One electrode was within, the other without, the cell. Currents of different intensities were sent through and the excess pressures were compensated and measured by raising and lowering a levelling arrangement. It was found that with one and the same cell the wind pressures were proportional to the current, but with different cells no agreement could be obtained. Results which should have been the same, only that different cells were used, varied in some instances as 1 : 76. The author sees in this a proof that the kinetic theory of gases is not applicable to solutions. The formula by which the wind pressures of the ions should be calculable, provided the kinetic theory of gases can be applied to solutions, is developed at length. The results obtained are entirely different from those calculated. This is considered as a further proof that the kinetic theory does not hold. It is stated that every possible source of error or difference in the construction of the cells and the membranes has been considered. It would have been interesting if this point had been discussed at greater length and it would at the same time have made the final conclusion more convincing. It is agreeable to find so explicitly stated what van 't Hoff has said, that whether substances in solution conform to the kinetic theory or owe their properties to an attraction between the molecules of solvent and solute, or to anything else whatever, his laws of solutions hold good and are not affected in the least ; anymore than the gas laws would be disproved if future experience causes us to abandon the kinetic theory of gases. *S. L. B.*

On the osmosis of liquids through a rubber membrane. *G. Flusin. Comptes rendus,* **126,** *1497 (1898).* — The author was unsuccessful in his attempt to measure osmotic pressure with a rubber diaphragm, though we are not told what the difficulty was. He then measured the rate at which different substances diffuse through the rubber into ethyl alcohol and compared these rates with the solubility of the same substances in rubber. It was found that the two sets of observations did not run parallel and that the important factor is the rate of solution, not the total solubility. *W. D. B.*

On the absorption of halid salts of potassium by plants. *E. Demoussy. Comptes rendus,* **127,** *771 (1898).* — Potassium chlorid and potassium bromid are absorbed very rapidly up to a certain point by colzas. These salts cannot be washed out by cold water while the plant is living. They can be washed out of the living plant by boiling water and can be extracted with cold water if the plant be first killed by chloroform or ether. Potassium iodid is not absorbed. One would be glad to see this matter studied carefully with reference to the osmotic pressure phenomena. *W. D. B.*

Selective absorption of some salts by plants. *E. Demoussy. Comptes rendus,* **127,** *970 (1898).* — From a mixture of potassium nitrate and chlorid a great excess of nitrate was taken by the young plants even though the chlorid was present in excess in the original solution. From a mixture of potassium and calcium nitrates in equivalent quantities an excess of potassium nitrate was absorbed. With potassium and sodium nitrates practically no sodium salt

was absorbed. With sodium and calcium nitrates nearly equivalent quantities were absorbed, one salt or the other predominating slightly, depending on the nature of the plant. *W. D. B.*

On a Crookes tube with an osmotic diaphragm. *P. Villard. Comptes rendus*, **126**, *1413* (*1898*). — A platinum tube is fastened to a Crookes tube, the whole filled with hydrogen and sealed. On heating, the hydrogen diffuses out forming a vacuum. By placing the tube in an atmosphere of hydrogen, the pressure inside the tube can be increased. *W. D. B.*

On the diffusion of gases through water and through agar jelly. *G. Hüfner. Zeit. phys. Chem.* **27**, *227* (*1898*). — With an ingeniously constructed apparatus in which a thin plate of hydrophane (a mineral through which gases can pass but which is impervious to water) was used, the diffusion constant K of ammonia was determined at various temperatures. The values obtained are K_0 0.727, K_5 0.822, K_{10} 0.953, K_{15} 1.106, K_{20} 1.250. In calculating these values Bunsen's absorption coefficients were used. The results differ somewhat from those of Scheffer; they are very different from those of J. Müller; but they agree well with Voigtländer's determinations in agar jelly. If the influence of temperature is expressed by means of Voigtländer's equation $K_t = K_0(1 + \alpha t)^2$, the above determinations yield the value 0.026 for α. As the values found are only one-half as large as those calculated according to Exner's law from the rate of diffusion of carbon dioxid, they indicate the presence of a double molecule.

In agar jelly K was found to be 3.75 at 10°, which seems to agree well with the values previously found by means of the hydrophane method, viz.: K_{16} 4.09, K_{21} 4.45. The influence of temperature on the speed of diffusion of carbon dioxid through agar jelly was tested. Using the equation $K_t = K_0(1 + \alpha t)$ α being found to be 0.10295. From the rate of diffusion of carbonic acid the values of K for a number of organic and inorganic acids and for the hydroxids and chlorids of the alkalies and alkaline earths were calculated according to Exner's law. The figures thus obtained do not agree with those found experimentally by Voigtländer. The latter's results yield molecular weights indicating polymerization of the molecules of the organic acids tested, the coefficients of association of the latter being as follows: formic 3.46, acetic 5.60, propionic 6.74, butyric 7.88, oxalic 2.90, tartaric 2.15, citric 3.192.

The author compares directly the diffusion of non-electrolytes with that of electrolytes, which is not allowable according to the views commonly accepted at present. *L. K.*

Velocities

On the velocity of solidification. *H. A. Wilson. Proc. Camb. Phil. Soc.* **10**, *25* (*1899*). — The present paper has for its object the explanation of the peculiar shape of the velocity-supercooling curve for liquids. When the supercooling is very small the velocity increases very slowly. As the supercooling is increased the velocity increases more rapidly and then becomes constant for a considerable distance. When the supercooling is very great the velocity becomes small and may even fall to zero. From elementary considerations the author deduces the expression

$$\omega = \frac{F}{A\alpha}\,\frac{\theta_0 - \theta}{\theta_0}$$

to represent the velocity of solidification or the rate at which the tip of the ray of solid travels out in a supercooled solution. Here F is the latent heat of fusion; A is the force required to give unit velocity to one gram of the liquid diffusing through itself; α is the thickness of the surface of separation; $\theta_0 - \theta$ is the degree of supercooling. Then as ω passes through a maximum value on account of the rapid increase of A as the temperature falls and taking θ_1 as the temperature corresponding to this maximum, two considerations, when the supercooling is greater and when less than $\theta_0 - \theta_1$, are sufficient to account for the observed relation between the supercooling and velocity. The rest of the paper is devoted to the general problem of solidification: "Given the distribution of solid and liquid and the temperature throughout a given space at any time and also the boundary conditions, to find the distribution at any subsequent or previous time." Two special problems are treated in detail and serve to illustrate the methods of studying such questions. *H. T. B.*

On the rate of crystallization. *A. Bogojawlensky. Zeit. phys. Chem.* **27,** *585 (1898).* — The author has determined the rate of crystallization at different temperatures of benzil, sulfonal, acetanilid, benzoin, mannit, santonin, picric acid, antipyrin, cumarin, erythrite, trichloracetic acid, peucedamin, salipyrin, cotoin, dinitrophenol, benzamid, menthol, dinitrotoluol, *m*-dinitrobenzoic acid, and *m*-dinitrobenzene. With all of these substances more than twenty degrees supercooling is necessary in order to reach the point at which the rate of crystallization begins to be independent of the temperature; with antipyrin sixty degrees supercooling being needed. Experiments were also made on mixtures of benzophenone and of sulfonal with benzil. *W. D. B.*

Velocity of sugar inversion in mixtures of alcohol and water. *Ernst Cohen. Zeit. phys. Chem.* **28,** *145 (1899).* — Experiments were carried out on the rate of inversion of 10% sugar solutions in pure water, in 50% and in 20% (by volume) alcohol with hydrochloric acid of concentrations varying between 1/2 and 1/128 normal. Great care was taken to have the temperature very constant at 18° both in the thermostat where the inversion took place and in the polariscope where it was measured. The constants were calculated according to the usual formula,

$$K = \frac{1}{t} \log \frac{A}{A - x}.$$

The rate of inversion in 50% alcohol was less than that in water. The ratio between the constants for dilute alcohol and for water increased with decreasing concentration of hydrochloric acid until it reached a maximum at about 1/32 normal acid where its value was 1.47. In other words sugar in 50% alcohol is inverted about two-thirds as fast as in water by hydrochloric acid not stronger than 1/32 normal. In the series with 20% alcohol the ratio between the constants reached a maximum with 1/8 normal HCl and had a value of 1.03. The author has shown in a previous article, Ibid. **25,** 42, that strong electrolytes are as completely dissociated in alcoholic solutions, up to 60% by volume of alcohol, as in water. Hence the difference in the rates of inversion cannot be attributed to different concentrations of the hydrogen ions, but must be explained by an influence of the solvent on the reaction. No hypothesis is advanced as to what the cause of this influence may be. *S. L. B.*

The reaction between potassium persulfate and potassium iodid, and catalysis in connection with the reaction. *T. S. Price Zeit. phys. Chem.* **27,** *474 (1898).* — The speed of the reaction, $K_2S_2O_8 + 2KI = 2K_2SO_4 + 2I$ or $S_2O_8'' + 2I' = 2SO_4'' + I_2$ was studied at 25°. From the second equation above it appears that the reaction should be of the third order, but the "constants" calculated on this assumption increase regularly; much better results are obtained by applying the equation of reactions of the second order to the experimental data. An application of van 't Hoff's formula for determining the order of a reaction yielded the result 2.4. When equivalent changes in the concentrations of the reacting substances are made, the time in which one-third of the change takes place remains practically constant, from which the author decides that the reaction is of the second order. No explanation is given as to why the reaction does not conform to the equation of the third order.

The presence of the following substances accelerates the reaction, $FeSO_4$, $FeK(SO_4)_2$, $CuSO_4$; while those that have little or no effect are HNO_3, H_2SO_4, FeF_3, $K_2Cr_2O_7$, CrO_3, $NaNO_2$, $MnSO_4$, $CoSO_4$, $NiSO_4$,$ZnSO_4$, $MgSO_4$, K_2SO_4, Na_2SO_4, $(NH_4)_2SO_4$, MoO_3, V_2O_5. Ferrous sulfate is more active in acid than in neutral solution; the reverse is true of copper sulfate. The catalytic agents act in proportion to their concentration. When ferrous sulfate and copper sulfate are both present, their combined effect is nearly double that calculated on the assumption that their influence is simply additive. The action of ferrous and copper sulfates is but slightly changed by the addition of zinc or manganese sulfate. Ferrous and copper sulfates also accelerate the reaction when potassium bromid is used in place of potassium iodid, while when sulfurous acid is employed their action is nil, or at any rate very slight. *L. K.*

The velocity of the reaction between silver acetate and sodium formate. *A. A. Noyes and G. T. Cottle. Zeit. phys. Chem.* **27,** *578 (1898); Jour. Am. Chem. Soc.* **21,** *250 (1899).* — The reaction between silver acetate and sodium formate may be represented by the equation $2CH_3CO_2Ag + HCO_2Na = 2Ag + CO_2 + CH_3COOH + CH_3CO_2Na$ or the equation $2Ag^+ + HCO_2^- = 2Ag + CO_2 + H^+$. The sodium salt of formic acid and the silver salt of a weak acid were chosen for the purpose of reducing the catalytic action of hydrogen as ion to a negligible minimum. In each of the seven series the values of the constant were more satisfactory on the assumption that the reaction is trimolecular than on the assumption that it is bimolecular. When the different series are compared, there can be no doubt but that the reaction is of the third order. The constant is a trifle less satisfactory when the initial concentration of the silver salt is changed than it is when the concentration of the sodium formate varies. Though the reason for this is not definitely established the authors incline to the hypothesis that it is connected with the electrolytic dissociation of silver nitrate.

W. D. B.

On the velocity of electrical reaction. *E. Cohen. Proc. Roy. Acad. Amst.* **1899,** *334.* — Taking a transition cell of the third kind, the author proposes to measure what he calls the velocity of electrical reaction. The study given in this paper is for $ZnSO_4.7H_2O$ and $ZnSO_4.6H_2O$ below the inversion point, 39°.

The cell is composed of two Clark cells connected in parallel, one of which contains the stable phase of the salt and the other the metastable. The current which is set up in the transition cell represents the velocity of reaction and the E. M. F. determines the maximum work the reaction at any temperature can perform. The author calls K this velocity constant and it is of course represented by

$$K = \frac{E}{R_1 + R_2}$$

where R_1 and R_2 are the resistances of the two Clark cells. Taking the direct measurements given by Jaeger, the author finds that on plotting the values of K with the temperature starting from 39°, the velocity of electrical reaction rapidly increases, reaches a maximum at about 9° and then diminishes again. The author states that it is worthy of note that the curve here represented possesses the same form as that showing the rate of crystallization of many substances at temperatures below the melting-point. The paper is one of considerable interest and the further work promised for other combinations will be looked for. *H. T. B.*

Rate of saponification of phosphoric esters. *J. Cavalier. Comptes rendus*, **127**, *114* (*1898*). — At 88° in tenth-normal solutions the reaction is monomolecular. The methyl esters are decomposed about twice as rapidly as the ethyl esters. The tri-ester is decomposed much the most rapidly and the di-ester the least rapidly. The tri-ester is decomposed more rapidly by bases than by water; but the reverse is the case for the other two esters. *W. D. B.*

Reaction velocities. *A. von Hemptinne and A. Bekaert. Zeit. phys. Chem.* **28**, *225* (*1899*). — Measurements were made of the velocity of the reaction between triethyl amin and ethyl bromid in different solvents and in mixtures of different solvents. The temperature was maintained constant at 66°. The article amounts to a continuation of Menschutkin's work with this same reaction. The velocity constants were calculated according to the usual formula for bimolecular reactions,

$$Ka = \left(\frac{a}{a-x}\right)t.$$

The pure solvents used were, benzene, acetone, chlorbenzene, benzyl, methyl, ethyl and propyl alcohols, xylene, ethyl alcohol + 2 % water, and acetone + 10 % water. The reaction went fastest in benzyl alcohol and slowest in xylene. Mixtures of two of these pure substances were then used as the solvent. In some cases the velocity of the reaction in the mixture was what it should be calculating simply from the amounts of each solvent present and the values for the pure substances (within the limits of experimental error). In other cases the reaction went much faster than was to be expected from this method of calculation; in others yet the velocity was less. When the two solvents belong to the same class of compounds the velocity found is close to the velocity calculated When the two solvents belong to different classes the velocity found may be less and often is more than the velocity calculated. Where great differences occur between the values found and calculated it is noticed that one of the solvents contains an hydroxyl group. A few experiments were carried out with mixtures of three substances as solvent. Generalities are not apparent in these results. *S. L. B.*

Non-explosive decomposition of guncotton and test for stability. *C. Hoitsema. Zeit. phys. Chem.* **27,** *567 (1898).* — By keeping Dutch guncotton for five hours below 160° and then raising the temperature slowly to 210°, it was converted into a mixture of gases and a solid mass which was no longer explosive. The composition of this residue was C 31 %, H 5 %, O 57 %, N 7 %, while the composition of the gas given off was approximately CO_2 36.2, NO 25.2, CO 17.9, H_2O 9.8, NO_2 1.4 and N 9.5, expressed in volume percentages. It is to be noticed that there is only a small quantity of any oxid of nitrogen with the exception of NO. The author is of the opinion that with pure guncotton no NO_2 is formed as a primary product. As a test for purity, therefore, he proposes to observe the time before a reaction for NO_2 can be detected when the guncotton is heated at some definite temperature. Results by this method are compared with those obtained by the methods of Abel and of Guthmann, and the new method stands the test well. The author feels that there are not enough experiments to enable him to state what should be taken as the standard temperature.

W. D. B.

On the limits of inflammability of carbon monoxid. *H. LeChatelier and O. Boudouard. Comptes rendus,* **126,** *1334 (1898).* — The normal limits of inflammability are for a mixture containing 16 to 74.5 percent carbon monoxid. These measurements were made in tubes having an internal diameter of 40 mm. Decreasing the diameter brings the limits nearer together, no mixture being inflammable in tubes with an internal diameter of 2.3 mm or less. Decreasing the pressure has the same effect; at 80 mm of mercury all mixtures cease to be inflammable. Increasing the temperature increases the inflammability. The conflicting results obtained by Rozkowski are attributed to slow combustion before making the test. The inflammability of mixtures of carbon monoxid and acetylene could not be calculated with accuracy from the limiting values for the single gases. *W. D. B.*

On the limits of inflammability of combustible vapors. *H. Chatelier and O. Boudouard. Comptes rendus,* **126,** *1510 (1898).* — The authors have determined the limiting concentrations at which thirty-one substances are inflammable when mixed with air. With the exception of hydrogen and of carbon bisulfid, the heats of combustion of 23.5 liters of these limiting mixtures do not vary much from 12.5 cal. The limiting concentrations appear, as a rule, to be such as to require 11.5 percent in volumes of oxygen for complete combustion.

W. D. B.

Electromotive Forces

On the thermoelectric forces in crystallized bismuth. *L. Perrot. Comptes rendus,* **126,** *1194 (1898).* — The author has measured the thermoelectric force of the couple bismuth-copper when the surface of contact was parallel to the main cleavage plane of bismuth and when it was perpendicular to it. The electromotive forces in the first case are more than double those in the second case; but the increase with increasing temperature-difference is greater when the surface of contact is perpendicular to the main cleavage plane than when it is parallel with it. *W. D. B.*

Studies on polarization capacity. *A. M. Scott. Wied. Ann.* **67,** *388 (1899).* — There is nothing very startling in the present paper. It appears to be a simple straightforward account of certain experiments conducted with a view to enlarging the knowledge of polarization capacity. The method adopted is the Wheatstone bridge method of comparing condensers. The results of the work are summed up by the author, and show sufficient variance to be interesting. It appears that the polarization phenomenon in thin gold membranes is to be explained by minute pores in the metal, which is not shown by platinum leaf. The polarization capacity of polished platinum is determined by the occluded gases, and depends on the condition of the platinum. Gold and aluminum behave similarly with cathodic polarization and show an increase with the E. M. F. With anodic polarization aluminum forms an insulated layer while gold goes into solution. The polarization capacity of Ag and Pb is conditioned by the metal ion in the electrolyte. Mercury under cathodic polarization has a minimum capacity with the E. M. F. which corresponds with the potential difference between it and the electrolyte. Outer pressure exerts no influence on the polarization capacity. *H. T. B.*

On the degree of magnetization of water. *G. Jäger and St. Meyer. Wied. Ann.* **67,** *427 (1899).* — N. DuBois pointed out in a recent note that the difference between the results of the authors and his own, for the magnetic susceptibility of water, must be due to an erroneous determination of the former's field strength. The authors have made special determinations of the field strength used by them and find sufficient agreement by different methods to justify their former calculations. The present paper is a reply to DuBois and also to state that after careful consideration they fail to be able to explain the huge discrepancy between their results and those of DuBois and the more recent ones of Königsberg. *H. T. B.*

Electrolysis and Electrolytic Dissociation.

On the use of the silver voltameter and its application to the determination of standard cells. *K. Kahle. Wied. Ann.* **67,** *1 (1899).* — This is a reprint of a paper published by the author in the Zeit. Instrumentkunde, **18,** 229 (1898). It is a careful study of the silver voltameter undertaken with a view to determining just how far it can be relied on as a standard instrument. This naturally follows the author's extended work on the Clark cell. Questions as to the character of the depositing dish, uniformity and method of washing the silver deposit, the neutrality or acidity of the $AgNO_3$ solution are of course dealt with at length.

There is no way in which the author's method of procedure essentially differs from that already given by Lord Rayleigh. He does not think the errors arising from the retention of $AgNO_3$ in the pores of the deposit amount to anything if it is washed three times with cold water and left to soak for one hour with water at 80°. A correction has to be applied for the solubility of the silver in hot water. This amounts to from 0.1 to 0.2 mg per hour.

Wide divergences in the results are found for different solutions and show the great caution required in using the voltameter. Differences of one in a thousand may easily be obtained unless the solution is kept strictly normal.

The author's final value is 0.0011183, which is in excellent agreement with Lord Rayleigh's original value 0.001118. This is in terms of the author's value for the Clark cell, 1.43285 volts at 15° C. The results of the work undoubtedly point to the enormous difference between the accuracy of the silver voltameter and the Clark cell for determining the unit of current. The latter has been brought to such a high state of perfection that there seems little object in clinging to or even considering the silver voltameter as a standard instrument.

H. T. B.

On the production by electrolysis of crystallized tungsten. *L. A. Hallopeau. Comptes rendus*, **127**, *755 (1898)*. — If fused paratungstate of lithium be electrolyzed between platinum electrodes there is formed a mass of crystallized tungsten mixed with platinum, this latter being due to the action of lithium on the electrodes. *W. D. B.*

Polarization and internal resistance of electrolytic cells. *K. E. Guthe. Phys. Rev.* **7**, *193 (1898)* — The author gives in this paper certain preliminary results as to the possibility of representing mathematically the change in the internal resistance of electrolytes with increasing or decreasing current. He proposes an empirical formula taken from Wiedeburg

$$R = \frac{E}{C} - \frac{P}{C}(1 - e^{-KC}),$$

where P and K are constants. If the resistance R is deduced from E, C alone it will always be too large. The author gives a brief description of his method and shows by means of a plot the excellent agreement of the observed values with those deduced from the expression given above. *H. T. B.*

Note on the experiments of I. Bosi on the resistance of moving electrolytes. *E. H. Hall. Phys. Rev.* **7**, *246 (1898)*. — The changes found by Bosi for the resistance of electrolytes in motion (**1**, 621) are brought into question by the author. Experiments under his direction for $CuSO_4$ show that no such effects recorded by Bosi are produced. If they are so they must be very much smaller than Bosi has given. *H. T. B.*

On the passage of the electric current through liquid dielectrics. *A. Naccari. Nuovo Cimento*, (*4*) **8**, *259 (1898)*. — It has been claimed that the specific resistance of petroleum varies with the electromotive force; but the author finds this not to be the case. He was also unable to confirm the report that the resistance is not a linear function of the thickness of the liquid layer.

W. D. B.

A new mercury voltameter. *L. Gurwitsch. Zeit. Elektrochemie*, **5**, *319 (1899)*. — By an elaborate system of stop-cocks, tubes and globes the author succeeds in measuring the increase in the amount of the mercury cathode by the rise of alcohol in a capillary tube. The advantage claimed for the instrument is that the resistance remains constant so that the apparatus can be placed in shunt if necessary. The instrument hardly seems simple enough to make it a valuable addition to the laboratory stock. *W. D. B.*

On the dissociating power of solvents. *J. W. Brühl. Zeit. phys. Chem.* **27,** *319* (*1898*). — The dissociating power of solvents is referred to the unsaturated condition of certain atoms contained in the solvent. In the case of solvents containing oxygen the latter is assumed to be quadrivalent and hence endowed with two spare valences; compounds containing trivalent nitrogen have dissociating power because the nitrogen has two spare valences. The fact that the molecules of solvents are polymerized in many cases is ascribed to the same cause. It is prophesied that other unsaturated solvents like the trichlorids of phosphorus and arsenic, the mercaptans and organic sulfids will be found to possess dissociating power. It is stated that the presence of spare valences is not sufficient to endow a solvent with dissociating power, but that these valences must be of a certain peculiar kind, which, however, is not further defined. It is simply pointed out that this is shown by the behavior of sulfur in carbon disulfid and carbon in the olefine series. As the molecules of the latter compounds polymerize readily, it is claimed that polymerization is in itself not a sufficient criterion and not the fundamental cause of dissociating power. In connection with the fact that hydrocarbons of the benzene series though unsaturated have no dissociating power it is stated that these hydrocarbons behave like saturated compounds in some respects.

The reader's attention is directed to an article on the same subject in the Jour. Phys. Chem. **3,** 12 (1899). *L. K.*

On the dissociation of polyvalent salts. *P. Calame. Zeit. phys. Chem.* **27,** *401* (*1898*). — The freezing-points and the electrical conductivity of aqueous solutions of salts of bivalent metals with mono-, di- and tribasic acids were determined and the degree of dissociation was calculated from the results. In the case of the copper salts the E. M. F. between the solutions and the metal was also determined. The formates of Sr, Ba, Ca, Cu and Zn are dissociated to nearly the same extent as the acetates of their metals. The formate of Mg, the acetates of Ni, Co, Cd, Pb, the propionates of Ba and Cu, the butyrate of Cu, the lactates of Ca and Cu, the salicylates of Ba and Ca, the maleinates of Mg and Zn, the fumarate of Mg and the malates of Mg and Cu were investigated in addition to the salts above mentioned. When the salts of the same anion are arranged with respect to their degree of dissociation, the order of the cations in the different series thus obtained is the same. The dissociation of zinc formate and acetate and of lead acetate increases more rapidly with the dilution than the dissociation of the other salts; the curves of these three salts therefore cut those of the others. The degree of dissociation of the acetates of the alkaline earths decreases between the concentrations N/2 and N/4 as the dilution increases. The malate, citrate and glycerate of copper form complex molecules in aqueous solution, while the salicylate and lactate do not. Magnesium fumarate is more strongly dissociated than magnesium maleinate, a fact that is explained by Ostwald's theory of the dissociation of dibasic acids.

The results show that the degree of dissociation of a salt is not determined solely by the "ionizing tendency" of the substances that become ionized, a view expressed by Ostwald, Lehrbuch, 2, 791. The author mentions the fact that according to the measurements of Arrhenius the degree of dissociation of copper chlorid is nearly the same as that of strontium and barium chlorids.

Barium and calcium are very high in the electrochemical series and copper is low. It is evident that this article adds to the number of facts which it is very difficult for the theory of electrolytic dissociation to explain. *L. K.*

On the taste of salts and alkalies. *R. Höber and F. Kiesow. Zeit. phys. Chem.* **27**, *601* (*1898*). — The salty taste of KCl, NaCl, $MgCl_2$, CH_3NH_3Cl, $C_2H_5NH_3Cl$, NaBr, NaI, K_2SO_4 and Na_2SO_4 depends on the anion and becomes noticeable at a concentration of 0.020–0.025 gram-ion per liter. Ammonium salts can be detected in solutions only one-half to one-third as concentrated as the preceding and this extra sensitiveness is believed to be due to the ease with which ammonium salts pass through animal membranes. The sweet taste of beryllium chlorid or sulfate can be detected at the point of the tongue in 0.00025–0.00045 normal solutions, the back portions of the tongue being less sensitive. Alkalies are said to have a sweet taste due to hydroxyl as ion. This can be recognized as soon as the concentration of hydroxyl as ion becomes 0.006–0.009 normal. See **3**, 66. *W. D. B.*

On the toxicity of copper salts with reference to the higher vegetables. *G. Bonnier. Comptes rendus*, **127**, *400* (*1898*). — It appears that about a *n*/3000 solution of bromid, chlorid, sulfate, acetate or nitrate of copper is required to kill a germinating wheat plant. Since the results with the different salts correspond within the limits of experimental error, we are here dealing with the toxic action of copper as ion. *W. D. B.*

The toxic effect of chromium compounds on the higher vegetables. *H. Coupin. Comptes rendus*, **127**, *977* (*1898*). — Chromium is much more toxic as chromate or bichromate than as chromic sulfate or chrome alum. Chromic acid is more toxic than the salts and the bichromates are more toxic than the chromates. The experiments do not appear to be accurate because it is said to take twice as concentrated a solution of sodium chromate as of potassium chromate to kill young wheat plants while the limiting solution of potassium bichromate is five times as concentrated as that of sodium bichromate. The concentrations are given in grams per hundred grams of water. *W. D. B.*

Formation of salts in alcoholic solution. *S. Tanatar and B. Klimenko. Zeit. phys. Chem.* **27**, *172* (*1898*). — According to the dissociation theory, the heat of neutralization of acids and bases in water solution is the heat of formation of undissociated water from its ions. In alcohol solution dissociation is much less, therefore the heat of neutralization in this solvent must be different from that in water. If ammonia is the base, the heat of neutralization must be quite different as then no water at all is formed. The authors carried out a few experiments neutralizing benzoic and lactic acids with ammonia and with potassium hydroxid, all 1/10 normal solutions in alcohol. The heat of neutralization was observed in a Berthelot calorimeter. They find the heat of neutralization of either acid with ammonia about twice what it is with potassium hydroxid. They also find the heat of neutralization with potassium hydroxid considerably less in alcohol than in water solution. They determined the specific heats of alcohol and of the solutions they used, also the heats of solution of benzoic acid, ammonium benzoate and potassium benzoate. *S. L. B.*

On a method of facilitating the measurement of temperature by means of platinum thermometry. *G. B. H. Wade. Proc. Camb. Phil. Soc.* **9,** *526 (1898).* — In speaking of the method of measuring temperatures by the use of platinum thermometers the author says: "Probably one reason why it is not more frequently used is that equal increments of resistance do not represent equal increments of temperature, so that inconvenient calculation are required to deduce the latter. The object of this paper is to describe a means of avoiding these calculations". In order to do this the method adopted is certainly ingenious, but it is difficult to see wherein it could be more simple than the ordinary method of reduction. Instead of compensating the change of resistance by one set of coils on a Wheatstone's bridge the author proposes to use a shunt of two sets of coils such that "by whatever amount the resistance of one arm of the shunt is increased, that of the other is to be diminished." It is easily seen then that by suitable arrangement of resistances, and as the sum of the resistances in the shunt remains constant then the arms of the shunt are linear functions of the temperature. After proving the corrections of the assumption some examples are given showing the applicability. In conclusion the author remarks that as the resistance of a perfectly pure piece of platinum wire might be a linear function of the temperature, it would be possible to regard the impurities as a sort of shunt in providing an alternative path to the passage of the current. *H. T. B.*

On the electrical resistance of steel. *H. LeChatelier. Comptes rendus,* **126,** *1709 (1898).* — The electrical resistance of steel increases with increasing amounts of carbon, silicon, manganese or nickel. Tungsten and molybdenum have little effect. *W. D. B.*

Influence of tempering on the electrical resistance of steel. *H. LeChatelier. Comptes rendus,* **126,** *1782 (1898).* — Tempering below 710° has no effect upon the electrical resistance of carbon steel. Tempering above 710° increases the resistance, there being an increase of two hundred percent when the steel is tempered at 950°. The presence of chromium increases the effect due to the temperature at which the steel is tempered while the presence of tungsten decreases it. *W. D. B.*

Electrical resistance at the point of contact of two discs of the same metal. *E. Branley. Comptes rendus,* **127,** *219 (1898).* — A column of zinc or copper discs has the same resistance whether the discs be superposed quietly or by dropping; but this is not the case with aluminum, iron or bismuth. With aluminum the resistance was sometimes greater by two hundred ohms when there had been a series of shocks than when the discs had been piled up quietly. No explanation is offered. *W. D. B.*

Dielectricity and Optics

On the dielectric constant and electrical conductivity of liquid ammonia. *H. M. Goodwin and M. deK. Thompson, Jr. Phys. Rev.* **8,** *38 (1899).* — The results of Cady on "The Electrolysis and Electrolytic Conductivity of Certain Substances Dissolved in Liquid Ammonia" (**1,** 707) have induced the authors to study the dielectric constant and conductivity of liquid ammonia. The re-

sults of their work on the dielectric constant by Drude's method show a much smaller value (22) than for water (80) which should not be the case if, as seems likely, liquid ammonia has a higher dissociative power than water. If corrections are applied for the wide divergence in temperature between water and liquid ammonia the discrepancy becomes worse. The results for the conductivity show between $-30°$ and $-12°$, an increase of 0.7 percent per degree and a specific conductivity of about 1.6×10^{-4}. The experiments on $AgNO_3$ confirm the results of Cady and make the molecular conductivity greater than in water. *H. T. B.*

Variation of the dielectric constant of glass by mechanical stress. *G. Ercolini. Rend. Accad. Lincei,* (5) **7,** *II, 172, 183* (*1898*). — After a discussion of the different theoretical views the author describes his own experiments. His results confirm the theory of Lippmann that the dielectric constant of glass increases under mechanical stress. For small weights the increase is not quite proportional to the weight; but this relation is very nearly true for larger weights. *W. D. B.*

Variation of the dielectric constant of rubber by mechanical stress. *O. M. Corbino and F. Cannizzo. Rend. Accad. Lincei,* (5) **7,** *II, 286 1898.* — The dielectric constant of rubber decreases under mechanical stress. *W. D. B.*

On the variation of dielectric constants with the temperature. *H. Pellat and P. Sacerdote. Comptes rendus,* **127,** *544* (*1898*). — The dielectric constant of paraffin decreases with rising temperature while the reverse is true for ebonite. This may introduce serious errors in determining the energy of a condenser. *W. D. B.*

Influence of the surrounding dielectric on the conductivity of copper. *J. F. Merrill. Phys. Rev.* **8,** *112* (*1899*). — The author meritoriously undertakes to settle the question of the influence of surrounding dielectrics on the conductivity of copper wire. There could of course be but one outcome of his work, if it had been correctly performed, and that is a negative one. He found within the limits of error of his measurements, 0.01 percent, that the character of the surrounding dielectric has no effect on its conductivity. Hence "a necessary modification of Ohm's law" must be regarded as unsubstantiated, unwarranted and absurd. *H. T. B.*

On the connection between the chemical composition of a gas and the ionization produced in it by Röntgen rays. *J. J. Thomson. Proc. Camb. Phil. Soc.* **10,** *10* (*1899*). — In Röntgenized gas the limiting value of the current between two electrodes, reached after an indefinite increase in the E. M. F., shows that the number of ions produced by the passage of the current just equals the number used up. The author makes a study of the saturation currents for different gases under the influence of Röntgen rays to obtain the degree of ionization. By having two tubes exposed to the rays at the same time, one with air and the other with gas, all errors due to the varying intensity of the rays are eliminated. The results are then expressed in terms of air. The results show that the ionization of a compound gas with the exception of cyanogen obeys the additive law and may be calculated with close approximation. "If $2[A]$, $2[B]$

represent the ionization of the elementary substances A_2, B_2 respectively, the ionization of the compound gas represented by the formula A_pB_q will be equal to $p[A] + q[B]$". This law is amply verified by the experimental results. In the case of cyanogen the author points out that the discrepancy from the additive relation here is similar to that for the same gas in Kopp's law of volumes.

H. T. B.

The optical activity of gallotannic acid. *O. Rosenheim and P. Schidrowitz. Jour. Chem. Soc.* **73,** *878 (1898).* — The authors confirm the statement of Walden that so-called 'pure gallotannic acid' is not pure. The commercial acid has a rotatory power varying from $[\alpha]_D = +11°$ up to $[\alpha]_D = +75°$. From all these acids they were able to separate an acid having a value $[\alpha]_D = +75.2°$. This they believe to be pure gallotannic acid, the lowering of the value in the commercial article being due to impurities, chiefly gallic acid. The derivatives obtained from all the commercial gallotannic acids are identical in rotatory power *inter se* and also with those prepared from the purified gallotannic acid.

Incidentally the authors have determined the solubility of gallic acid in various solvents and have noticed that three liquid phases are formed when water, acetone and ether are added to a mixture of gallic and gallotannic acids. The lowest layer was a syrupy concentrated solution of gallotannic acid containing a small quantity of ether; the middle one, an acetone solution rich in gallic acid, with a little gallotannic acid, the upper layer being an ethereal solution containing small quantities of gallic and gallotannic acids. *W. D. B.*

The influences modifying the specific rotatory power of gallotannic acid. *O. Rosenheim and P. Schidrowitz. Jour. Chem. Soc.* **73,** *885 (1898).* — In aqueous solutions containing up to one percent of gallotannic acid, it appears that the rotation is constant at $[\alpha]_D^{15°} = +75.2°$. The deep color of the solutions prevented satisfactory readings being made with more concentrated solutions. In all the organic solvents tested the rotation was cut down enormously, becoming zero with one mixture of acetone and carbon tetrachlorid. Gallic acid has no effect. Alkalies decrease the rotation and acids have no effect, beyond restoring the rotation when added to an alkaline solution. The borates and tungstates reduce the rotation enormously, carbonates somewhat, and chlorids very little. *W. D. B.*

On the flame-spectrum of mercury and its bearing on the distribution of energy in gases. *G. D. Liveing. Proc. Camb. Phil. Soc.* **10,** *38 (1899).* — The author announces the discovery of another mercury ray developed in the mercury spectrum of wave-length 4358. The presence of the ultraviolet ray λ 2535.8 was pointed out some time ago by the author in conjunction with Dewar for mercury heated in the electric arc. In the present case the author heats mercury in a cyanogen flame burning in oxygen. The emission of these two rays as the author says "in a flame where the stimulus appears to be only the high temperature since mercury is not known to combine with either oxygen, carbon or nitrogen at such a temperature, seems to be a fact of some theoretical interest." This being so the rest of the paper is of course of a more or less speculative nature. *H. T. B.*

On the comparative color of the vapor of iodine in air at atmospheric pressure and in vacuum. *J. Dewar. Proc. Camb. Phil. Soc.* **10**, *44* (*1899*). — The author finds not only does iodine vapor have a perceptible color but a distinct difference in color in the vapor at different pressures. He also finds that iodine distilled and condensed on a glass surface at — 182° in vacuum test-tubes shows transparent films of varying grades of thickness. These show brilliantly the colors of thin plates by reflection. *H. T. B.*

Spectrum analysis of some non-conducting minerals by means of melted salts. *A. de Gramont. Comptes rendus*, **126**, *1513* (*1898*). — Lithium, sodium, rubidium, cesium, calcium, strontium, barium, magnesium, manganese, chromium, aluminum, vanadium and zirconium, are easily recognized by this method, potassium and glucinum less readily while the method is not applicable to iron and nickel. *W. D. B.*

Observations of some spectra: aluminum, tellurium, selenium. *A. de Gramont. Comptes rendus*, **127**, *866* (*1899*).—Attention is called to the fact that certain lines commonly attributed to aluminum, to selenium and to tellurium do not appear in the spectra when these metals are very pure. *W. D. B.*

On the radiations emitted by thorium and its compounds. *G. C. Schmidt. Comptes rendus*, **126**, *1338* (*1898*). — Some measurements on the emission of Becquerel rays by thorium compounds. *W. D. B.*

Phosphorescent mixtures formed with strontium sulfid. *G. R. Mourelo. Comptes rendus*, **126**, *904*, *1508* (*1898*). — Adding two and a half percent or more of strontium sulfid to inert substances like barium and calcium sulfates and heating the mixture to a cherry-red heat makes the entire mass phosphorescent. *W. D. B.*

On a property of fluorescent screens. *P. Villard. Comptes rendus*, **126**, *1414* (*1898*). — If the shadow of any opaque substance be cast upon a screen of barium platinocyanid by the X-rays, the image of the object will remain on the screen after the source of light has been cut off. This image can be obliterated by exposing the screen to ordinary light. *W. D. B.*

On the brilliancy of a source of light. *P. Jenko. Wied. Ann.* **66**, *1182* (*1898*). — Accepting the unit (meter candle) to be the brilliancy of one cm^2 of Bristol-board placed one meter away from a standard candle, the author compares various sources of light with this. He finds the strength of the Violle unit is equal to 1,008,200 meter-candles. A comparison of the reflected light from a number of white surfaces shows that in reality no surface appears absolutely white. Taking Bristol-board with a brilliancy of 1 its color is brownish:

Fresh fallen snow	1.05–1.11	yellowish
ZnO with 5 pct gypsum	1.169	bluish gray
White lead	1.207	reddish yellow
$MgCO_3$	1.29	yellowish green

The author remarks that only $MgCO_3$ shows a complete mat surface, and hence is equally clear at all angles. He recommends the use of this substance instead of paper or gypsum for the unit of brilliancy. *H. T. B.*

On a new standard of luminosity. *C. Féry. Comptes rendus,* **126,** *1192 (1898).* — It is proposed to use as standard the flame produced by acetylene burning in air from the end of a tube having an internal diameter of 0.5 mm. The intensity is rather a complicated function of the amount of gas burned per unit of time; on the other hand, it varies practically proportionally with the height of the flame when this varies between 10 and 25 mm. *W. D. B.*

On the radiation of incandescent mantles. *H. LeChatelier and O. Boudouard. Comptes rendus,* **126,** *1861 (1898).* — The authors have studied the Welsbach mantles. They find that the emissive power at the temperature of the incandescent mantle is different for different rays. The advantageous results are due to the fact that the emissive power is nearly unity for the blue, green and yellow rays; is less for the red rays and is, without doubt, very small for the ultra-red rays. The proportion of energy radiated in the form of visible rays is therefore very large though the absolute value is nevertheless below that of a black substance at the same temperature. On the other hand a black substance under the same conditions of heating would have a very much lower temperature and would therefore be much less luminous. *W. D. B.*

On the vaporization of iron at ordinary temperatures. *H. Pellat. Comptes rendus,* **126,** *1338 (1898).* — To show that the effect produced upon a photographic plate by a piece of iron was due to the volatility of the iron and not to the emission of rays, the author placed two little iron rings on a photographic plate, one being enclosed in a glass box. When the plate was developed, no image of this second ring was to be seen. *W. D. B.*

Crystallography, Capillarity and Viscosity

On the structure of alloys of iron and nickel. *F. Osmond. Comptes rendus,* **126,** *1352 (1898).* — When examined under the microscope iron containing 0–8 percent nickel looks much like iron containing no nickel. Iron containing 12–25 percent nickel consists of fibrous bundles and looks like cast steel; it is hard and magnetic. Iron containing 25–50 percent nickel is markedly crystalline. *W. D. B.*

On the constitution of ternary alloys. *G. Charpy. Comptes rendus,* **126,** *1645 (1898).* — A microscopical study of alloys containing tin, lead and bismuth shows that the three crystallize side by side. In no system yet studied has the author found any evidence of a ternary compound. *W. D. B.*

On the estimation of capillary constants with solidified drops. *A. Gradenwitz. Wied. Ann.* **67,** *467 (1899).* — The author shows that the method of estimating the capillary constant for solid drops is open to the objection that the drop either becomes elevated or depressed on its surface depending on whether the material expands or contracts on solidifying. This would cause uncertainty in determining the vertical height. Examples are given for mercury, water, tin and silver. *H. T. B.*

ON THE PARAANISALDOXIMES

BY H. R. CARVETH

During the past year there has been carried on in this laboratory the examination of a number of bodies occurring in two modifications, of which the one with the higher melting-point was the less stable. In every case examined it has been proved that the Duhem theory of permanent change as developed by Bancroft and systematized by the use of Phase Rule methods is able to explain the phenomena observed. For a further test of this theory the writer has examined the conditions of equilibria present with the paraanisaldoximes when the two modifications are regarded as forming a binary system and also when by the introduction of another substance, it is assumed that there is formed a ternary system.

The first work on paraanisaldoxime was done by Westenberger[1] who formed the compound by adding, to an aqueous solution of hydroxylamine hydrochloride, sodium hydroxide and then the calculated amount of anisaldehyde in alcoholic solution. The yellow oil resulting was taken up in ether, the ether evaporated and the solution crystallized over sulfuric acid. Recrystallization from alcohol and ligroin gave white leaves of M.P. 45° which were but slightly soluble in cold but quite soluble in hot water. Four years later Goldschmidt and Polonowska[2] made use of Westenberger's method, and obtained as a product long hard prisms of M.P. 61°. In 1889 Miller[3] precipitated a benzol solution of the oxime by ligroin, obtaining a white powder of M.P. 64°, soluble in hot water, ether and benzol. Other

[1] Ber. chem. Ges. Berlin, **16**, 2993 (1883).
[2] Ibid. **20**, 2407 (1887).
[3] Ibid. **22**, 2790 (1889).

references to the melting-point of the compound are given by Goldschmidt,[1] Beckmann,[2] Hantzsch,[3] and by Goldschmidt and Rietschoten,[4] the latter giving as the M.P. 63°, the former three observers 61°.

In 1890 Beckmann[4] discovered an isomeric form of the oxime, the one now called the *β* modification. This he made by forming the hydrochloride of the *a* oxime, treating this with sodium hydroxide and crystallizing. Since the *β* modification is less soluble than the *a* form in benzol, it was comparatively easy to effect a sharp separation by using benzol as the solvent. The product obtained is stated to have shown a constant melting-point of 130°–130.5° even on slow heating, which, it will be remembered, is in marked contrast with the benzaldoxime which attains its melting-point only on being heated very rapidly. When boiled with ether for a few hours or when heated with alcohol at 150°, the *β* form is changed into its isomer; but this reaction is said not to occur when the substance is heated with alcohol to 100° for one hour. Goldschmidt[5] in examining the *β* form describes it as having a melting-point of 133° and as being less soluble than the *a* in ordinary solvents, and states that it may readily be changed into the *a* form by heating above its M.P. of 133°.

This short résumé shows conclusively that the anisaldoxime does exist in two modifications which are capable of existence as solids at ordinary temperatures; that they possess melting-points and other properties which are distinct but that they are nevertheless readily convertible one into the other. To such cases as this the Duhem theory may be applied with great advantage, while without its aid the explanation given for the phenomena must be insufficient if not inaccurate.

The anisaldehyde used as starting-point in the research was the commercial product, aubépine, supplied to us by Messrs.

[1] Ber. chem. Ges. Berlin, **23,** 2163 (1890).
[2] Ibid. **23,** 1687 (1890).
[3] Ibid. **26,** 929 (1893).
[4] Ibid. **26,** 2087 (1893).
[5] Ibid. **23,** 2163 (1890).

Fritzche Bros., of New York. This was fractioned, the part coming over at 246°–247° (744 mm) being retained and refractioned in an atmosphere of hydrogen. The aldehyde obtained was shaken up with concentrated aqueous soda solution, and the theoretical amount of hydroxylamine hydrochloride added. After washing with cold water the first product showed a M.P. of 50°. This was consequently recrystallized a great number of times from ether until there were obtained beautiful white crystals of M.P. 63°. This when melted up in amounts of three to five grams showed but a very slight tinge of yellow, which subsequent crystallization failed to remove; moreover it was not found possible by repetition of the crystallizations to raise the M.P. of the product. It was found later that crystallization from toluene removed the colored impurities more rapidly than when ether was used as solvent.

The β modification was prepared from the oxime hydrochloride. This salt was itself made by passing dry hydrochloric acid gas[1] slowly into an ethereal solution of the oxime at temperatures ranging from 0°–20°. After the precipitated hydrochloride was filtered, washed with ether and dried, it was pulverized, put into ice-cold water and slowly neutralized by dilute cold solution of potassium carbonate. The solid oxime resulting was washed with cold water, dried and crystallized from benzene. In this way it was possible to obtain quite a large yield of the β from the α oxime. The former crystallizes in long needles and on fairly rapid heating showed a melting-point of 132°.

The slight discrepancies between the melting-points of both forms as given by different observers has caused us to investigate how much importance must be attached to the melting-points of this substance in particular as a means of confirming its purity.

The experiment was performed in the following manner. The substance was put into a capillary melting-point tube which

[1] The gas was dried by passing through sulfuric acid, towers of glass wool, and calcium chloride. Slight traces of sulfuric acid carried over in some of the first experiments gave rise to colored compounds whose nature was not investigated.

was then sealed. This was fastened by a rubber band to a thermometer and the latter was then immersed in a bath of liquid kept at its boiling temperature. The Beckmann boiling-point apparatus serves the purpose of a constant temperature bath admirably, while mixtures of the ordinary organic solvents with each other or with water give one a series of liquids whose boiling-points may be varied at will.

The results which were obtained were as follows:

1. *a* oxime at 62.8°—melted at once.
   a " " 61.8°—melted but not completely in 22 minutes.
   a " " 61.0°—melted in 55 minutes.
   a " " 58.9°—not melted in 135 minutes.
2. *β* oxime at 134.0°—melted in 30 seconds.
   β " " 130.0°— " " 53 "
   β " " 124.5°— " " 155 "
   β " " 121.0°— " " 253 "
   β " " 117.1°— " " 360 "
   β " " 109.5°— " " 930 "
   β " " 89.5°— " " 7200 "

Here, therefore, we have two modifications whose melting-points depend entirely on the time of heating. This is the probable explanation why the melting-point of the *a* is given by different observers at 61°, 63°, and 64°, and the melting-point of the *β* as 130° and 133°, assuming that the conditions under which each observer worked were the same, with the exception of the time required in melting.

The results given above are not of great value regarded as quantitative data, since the influence of the walls is one whose effect cannot be estimated: for example, the fact that the *β* oxime took 30 seconds to melt when plunged into a bath whose temperature was 134°, while the melting-point had previously been found at 132°, plainly shows that the time required for the conduction of the heat to the interior of the tube cannot be neglected. Nevertheless the results when plotted show that there

is being approached a limit of temperature below which melting would have been impossible. If the triple and eutectic points coincide, then this temperature will mark the limit below which melting is impossible. If, as in the present case, the eutectic point lies below the triple point and more toward the side of the β modification, then the lowest temperature at which the α will melt will be that of the triple point; the β modification, however, may melt at the temperature of the eutectic point, but if after being melted it is kept for some time at this temperature, it will again solidify, owing to the displacement of the equilibrium toward the side of the α modification.

Experiments were made, therefore, to ascertain the temperature of the triple point and the effect of the initial temperature of heating on the displacement of the equilibrium. The measurements were taken with the ordinary Beckmann freezing-point apparatus, including the air-jacket, cooling bath, platinum stirrer and thermometer. The latter was divided into tenths, and all readings given are corrected. Starting with an amount of material which was never less than ten grams, the writer melted the oxime, allowed it to supercool one or two degrees in the air or bath, then immersed it in the Beckmann cooling bath, whose temperature must lie not more than a degree below the freezing-point of the mixture, and stirred vigorously until the thermometer showed a constant maximum reading. When the supply of material is small, it is necessary to have the degree of supercooling as constant as possible for successive measurements, and also to have the temperature of the cooling-bath quite close to the freezing-point to be observed.

There was examined first of all, the α form which had previously shown a melting-point of 62.8°. It was heated to 64° for thirty minutes, then cooled and the freezing-point taken; then heated at 87° for the same time, cooled and freezing-point noted. Proceeding similarly with the initial temperature at 100°, 125°, and 142°, it was found that for three sets of readings the temperature at which the mass solidified was 54.20 with a mean variation of $\pm$ 0.15°.

To ascertain whether the final equilibrium attained was the same whether one uses as first material the *α* or the *β* crystals, we have heated the *β* form up to the point of fusion and immediately determined its freezing-point, which was found to be 54.2°. Successive meltings and freezings have shown this also to be constant at 54.20° ± 0.25°. In not a single case has there been found any indication of decomposition, either by change of color or by loss of weight. From these experiments the only conclusions which can possibly be drawn are that the initial temperature of heating—at least up to 142°—has no effect on the final condition of equilibrium, and that the same equilibrium is attained whether one starts with the *α* or the *β* form. The change of one modification into the other is therefore accompanied by little or no heat effect, a phenomenon which has already been observed in the case of acetaldoxime and benzaldoxime, and which may possibly apply to all the oximes.

It has been hoped that the complete equilibrium curve for the two forms might be determined, since the work of Cameron[1] implies this as a possibility. The *α* and *β* forms were taken in known amounts, which were then intimately mixed and put into small capillary tubes. The ends of the tubes were sealed and the melting-points taken in the ordinary manner. In but few cases would a repetition with a second tube similarly prepared give results which were at all in harmony with the first determination. The diameter of the melting-point tube especially had a great deal to do with the melting-point observed, this occurring at a lower temperature when the diameter of the tube was increased, if the heating were not too rapid. This is probably due to the influence of the walls in preventing the *β* form from dissolving up rapidly in the liquid mixture. The method used by Cameron is not an ideal one in any case, since the effect of the time factor is one which cannot be estimated. Moreover the immediate taking of the freezing-point will give but a poor check on the melting-point determinations, since there is, at present, no way of estimating the extent of displacement which

[1] Jour. Phys. Chem. **2**, 412 (1898).

occurs when the solid fuses, or of ascertaining whether the mass in the capillary is completely solidified.

That Cameron was able with the benzaldoximes to obtain results which agree with each other must have been due to the comparatively slow change of the β into the α form. With the anisaldoxime we have shown that even considerably below its M.P., it changes over into the α form, while after it has been once heated to its melting-point, its freezing-point falls immediately to 54.20°.

It has, therefore, been found absolutely impossible to obtain with any degree of accuracy the composition of the triple point. That at this point there is present a mixture and not pure α has been verified in the following way. The equilibrium mixture formed after melting the β crystals has been crystallized from benzene after it was shown that benzene had but a small effect on the equilibrium relations. There were deposited at first a very few crystals whose crystalline form and high melting-point showed them to be the β modification. This offers, therefore, confirmatory evidence of the statement that, at the stable triple point, both of the stereoisomeric forms co-exist in the melt.

It was now decided to ascertain what was the position of the eutectic point relative to the triple point. All that can be said is that it lies about 0.2° lower than the latter. This was proved by adding the β modification in very small amounts to the triple-point mixture, dissolving at temperatures below 56° and noting the freezing-point. The maximum depression was, as stated, 0.2°. The difference in composition between these two points must also be extremely small, since on cooling a large amount of the melted oximes it was impossible to observe the second—i. e. the eutectic point—by plotting time-temperature results. Here again the temperatures observed when different amounts of β were added could not be plotted satisfactorily owing to the change of one form into the other; for this reason all numerical results on this point are omitted.

After reaching the eutectic point it was possible by addition of the β form to have the freezing-point rise again, but never to

a greater extent than about 1.5°. The experiment requires a temperature below 60° for the complete solution of β in the liquid and a rapid determination of the freezing-point. Of course continued heating above 60° causes the freezing-point to fall rapidly to that of the triple point.

It was now thought desirable to examine the relations when a third component was present. In the first instance, a substance was chosen which could form a compound with one of the components, viz. hydrochloric acid. The oxime hydrochloride is usually obtained as a white crystalline powder by passing dry hydrochloric acid gas into an ethereal solution of the oxime, but it may also be obtained as fibres by evaporation of an ethereal solution. An attempt was made to see if the compound, like both forms of the oxime, would melt below the so-called melting-point. The method used is the same as was used with the oxime and the results are given below:

β oxime hydrochloride at	129.5°	—	melted.	
"	117.5°	"	in 5	minutes.
"	106.0°	"	" 25	"
"	99.3°	"	" 40	"
"	90.2°	"	" 100	"
"	82.0°	"	" 528	"

In every case the hydrochloride melted with decomposition, so that, from these results, no conclusions as to the existence or non-existence of a second modification would be justified.

A number of experiments were made in the hope of obtaining another hydrochloride. Carefully dried hydrochloric acid gas was passed into solutions of the oxime in ether, benzene, and alcohol at temperatures ranging from $-20°$ to $+60°$, but in all of these experiments the one product alone was obtained, viz. the β hydrochloride. Finally the gas was passed into the melted oxime at a temperature of 65°. The precipitate formed was washed with benzene and dried. It gave a melting-point of 117°. On boiling with benzene or on recrystallization from ether, however, it gave the melting-point of the β hydrochloride,

the other product of crystallization being the original oxime. It is very probable, therefore, that there is but one form of oxime hydrochloride.

This is not in accord with the views of Hantzsch[1] from whose paper the following translation is made: "If now ordinary anisantialdoxime and cuminantialdoxime in ether solution are changed by the action of hydrochloric acid gas into the hydrochlorides, and the dried precipitates are covered with excess of an ethereal solution of ammonia, then, after filtering off the ammonium chloride formed, there will be obtained the original anisantialdoxime of M.P. 61° or the original cuminantialdoxime of M.P. 58°; or, conversely, if one starts with the stereoisomeric synaldoximes, then under quite the same conditions there is obtained the original oxime, anissynaldoxime of M.P. 130° or cuminsynaldoxime of M.P. 110°. There result, therefore, the different stereoisomeric hydrochlorides

$$XC_6H_4CH \quad \text{and} \quad XC_6H_4CH$$
$$HO\ddot{N}HCl \qquad ClH\ddot{N}OH$$

which in external appearance and in chemical behavior may scarcely be distinguished from each other and which show their individuality only in the invariable regeneration of the oxime from which they are derived. *The change of the antialdoximes into the synaldoximes which has been mentioned does not therefore take place here, if, in splitting off the hydrochloric acid, water is perfectly excluded.*

"Moreover these derivatives of pentavalent nitrogen are much more labile than those of the trivalent element, that is, than the oximes themselves. If, for example, the hydrochloride of anisantialdoxime be covered with not too great an excess of ethereal ammonia, or, preferably, if dry ammonia gas be led into absolute ether in which the hydrochloride is suspended, then the filtrate leaves behind almost pure anissynaldoxime; the cuminsynaldoxime under the same conditions leaves behind the cuminantialdoxime; finally from either *p*-nitrobenzantialdoxime or

[1] Ber. chem. Ges. Berlin, **26**, 929 (1893).

p-nitrobenzsynaldoxime is obtained a mixture of both stereoisomers."

The results given above were sufficiently strange to warrant a repetition. It was found that in every case where the hydrochloride was precipitated from absolute ether—whether there was used a solution of the pure α, pure β, or of a mixture—and where dry ammonia gas was passed into an amount insufficient to precipitate all the hydrochloric acid as ammonium chloride, that the crystals which appeared first were those of the synaldoxime. When, however, an excess of the ammonia was used, the crystal product was a mixture, the α form predominating. It would therefore appear that the action of ammonia is directly opposite to that of the acid—the tendency of the former being to make the α the stable form, while the acid favors the formation of the β. This is in direct confirmation of the results of Goldschmidt and Roder[1] on the benzaldoximes, if we assume, as seems positive, that no ammonium salt of the oxime is possible. Perhaps also Hantzsch has laid too great stress on the presence of water as preventing the change of the anti- into the syn- forms when the experiments he quotes show that the change may take place even when water is entirely absent, if the ammonia is not present in excess.

In his work on the equilibria of stereoisomers, Bancroft[2] has included in his general treatment a discussion of the results which are to be expected in the system, α and β aldoximes and hydrochloric acid, if the β alone form the compound. It had been hoped that it would be possible to pass along the curve of stable equilibrium for the three-component system. This has not been realized owing to the tendency of the β hydrochloride to decompose.

Starting with the composition represented by the triple point, the writer added the oxime hydrochloride to this to the amount of two percent. This dissolved readily at about 70° and gave a freezing-point of 55.60°. Heating at 65° for some time

[1] Ber. chem. Ges. Berlin, **28**, 2013 (1894).

[2] Jour. Phys. Chem. **3**, 144 (1899).

lowered the freezing-point to 54.98°; but this was the lowest freezing-point obtainable. It was evident, therefore, that the curve of stable equilibrium, if it rises toward the stable triple point as required by the theorem of van Ryn van Alkemade, must have ended before the concentration of the hydrochloride has reached two percent. It is probable that the first addition of the salt had taken the system at once into the field where the β hydrochloride exists as solid phase. Further measurements confirmed this view but it was impossible to carry them far enough to be of service. The possibility of securing quantitative results in systems such as these is not very hopeful and until there are found cases where the change from one isomer into another takes place so slowly as to be measurable, qualitative data alone must suffice.

Experiments were now made to determine the effect on the equilibrium of a third component which does not react with either of the modifications. The solvents chosen were alcohol, acetone, benzol, toluol, xylol and petroleum ether. In all of these the β is the less soluble, and in every case it has been found that after heating the β form with these solvents in sealed tubes, the temperature of heating lying above that of the boiling-point of the solvent, and the time of heating being never less than an hour, the melting-point of the crystals left invariably lay lower than that of the β oxime. This proves that in all these solvents the reaction proceeds in such a manner as to form α oxime. It was noticed in repeating the work of Goldschmidt by heating three tubes of the β dissolved in absolute alcohol for one hour, that the melting-point of the crystal product (which, of course, was not crystallized fractionally) had fallen to 117°, 118° and 120°. Further heating for an hour and a half gave melting-points of 85°, 85° and 86.5° showing that the reaction which Goldschmidt noticed at 150° also occurs at 100°, although the velocity of change is lower.

In benzol and toluol solutions, the rate of change is quite low. The β boiled for three hours with benzol showed a melting point of 111°; when boiled for seventy minutes with toluol

a melting-point of 127°, and when a solution in acetone was boiled for two hours a melting-point of 62° was obtained. The temperature of heating when a solvent is present is not the only factor in determining the equilibrium, but the specific nature of the third component in respect to its solvent action on the two different forms must also play a very great rôle. The experiments with the benzol and toluol solutions, which have just been mentioned, explain why these solvents are so effective in the separation of the β from the α form—not merely is there a great difference in the solubility of the two forms in these solvents, but the rate of change of one form into the other is so slow as to allow of practically complete separation. It would have been interesting to have determined, further, whether the use of a solvent in which the β was the more soluble form would have reversed the stability of the modifications. Unfortunately there has been discovered no solvent which does not react with the β where the latter form was more soluble.

Attention may now be directed to the manner in which the results of the consideration of these different stereoisomeric forms may be adapted to laboratory experience.

(1) If one has in hand a product from which the different fractional crystallizations show always the same percentage composition, and the same melting-point, and which has a freezing-point different from the initial melting-point (decomposition excluded) there is then very strong evidence for the existence of two modifications of this particular compound. If the freezing-point lies higher than the melting-point, the product in hand is instable; if it lies lower, either the stable or instable forms may form the initial material. Under ordinary circumstances the stable form will be the one first discovered.

(2) The instable modification may not be discovered without making use of a third component. This may reverse the stability relations either by mere solvent action or by forming a compound. The first case is readily tested by examining the whole crystal mass left after complete evaporation of the solvent. Should the melting-point have changed at all, this is a proof

that the continued action of the solvent may produce a separation. That it does not change is no proof of the non-existence of the isomer.

Should no separation be possible in this way, make, if possible, an additive compound from the initial product, and ascertain if this also has a melting-point which varies with the time of heating, or which is different from the freezing-point (decomposition again excluded). If either of the latter phenomena are observed, the existence of a second compound is very probable.

In this compound the stability relations may be displaced. In this case, the choice of correct conditions as to how to split off the third component can be determined readily, the main point which is to be observed being that the reaction must take place at a temperature where the change of one form into another is not noticeable. The formation of the β modifications of benzaldoxime and paraanisaldoxime illustrates this case, the yields being greater the lower the temperatures at which these forms are isolated. The correct choice of solvent is essential, but at present there are no data which can be of any general service on this point.

It is possible that in the compound the stability relations may not be reversed. Even in this case it may be possible by working rapidly and at very low temperatures to obtain the instable compound and, as in the previous case, the instable modification of the original material.

We shall give only two references to illustrate these rules. Hill and Allen[1] in speaking of the melting-points of certain products state that they were taken "at ordinary speed," and to explain this refer back to an article by Hill and Palmer[2], where these scientists noted that monobrommaleic and dibrommaleic acids give different melting-points, according to the time of heating. For instance monobrommaleic acid melts in 0.7 minute, in a bath at 143°, in 1.3 minutes at 133°, in 4.5 minutes at 125°, in 8 minutes at 121°, and, according to Kekulé,[3] begins to soften

[1] Am. Chem. Jour. **19**, 666 (1897).
[2] Ibid. **10**, 422 (1888).
[3] Liebig's Ann. **130**, 6 (1864).

at 100°. Taken "at ordinary speed" the melting-point is given at 129°–130°. If decomposition does not take place, one who knows the Duhem theory could at once state that such behavior points plainly to the existence of an isomer. The probable explanation is that the other isomer is bromfumaric acid of M.P. 190°, that it is stable at the higher temperatures, and that the eutectic point lies below 100°. Similar statements might be made with respect to the mono- and dichlormaleic acids which also show melting-points varying with the time of heating.

That the solvent may be of service in discovering another form is shown very plainly by the work of Goldschmidt and Rietschoten[1] who examined the action of various reagents on the oximes. The latter were dissolved, usually in ether, and the reagent added. In the case where it was necessary to let the mixture stand for some time in order to obtain a solid product—when paraanisantialdoxime was treated with phenylcyanate or with orthotolylcyanate; when orthoanisaldoxime or cuminantialdoxime reacted with phenylcyanate or with ortho- or paratolylcyanate; paranitrobenzantialdoxime with orthotolylcyanate and metanitrobenzantialdoxime with orthotolylcyanate—not once is it recorded that a second modification was discovered. But in almost every case where the compound was precipitated at once when the reagent was added—phenylcyanate or orthotolylcyanate to paraanissynaldoxime, paratolylcyanate to both the anisaldoximes, there was always found an isomer. This latter was always discovered in the same way, viz. by boiling the precipitate with a solvent. In regard to the action of paratolylcyanate on metanitrobenzsynaldoxime we must note that a precipitate was formed but no mention is made of any attempt to discover the other form.

It appears strange that Goldschmidt and Rietschoten did not note the relations we have just discovered from a consideration of their own work. Had they chosen other solvents for their oximes, they undoubtedly would have discovered more of the isomers for which they were looking. For their paper

[1] Ber. chem. Ges. Berlin, **26**, 2087 (1893).

proves conclusively that sudden precipitation favors the instable modification; and from this the stable form may be very readily derived.

It follows, therefore, that papers such as the one just discussed offer absolutely no proof as to the non-existence of isomers of certain compounds, and all arguments in regard to constitution which have as their basis experiments showing that under one set of conditions certain isomers cannot exist, must be regarded as useless.

This means that, sooner or later, space formulae as a system of explaining physicochemical reactions may be attacked from the standpoint of the Phase Rule and the modern idea of the chemical potential.

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ON THE RELATION BETWEEN PRESSURE AND EVAPORATION

BY EDWIN H. HALL

Many years ago[1] Thomson showed that the maximum vapor pressure in contact with the concave surface of a liquid, elevated by capillary action, must be less than the maximum pressure over a flat surface of the liquid at the same temperature. Maxwell's reference to this matter leaves it to be supposed that the diminution of vapor-pressure is due directly to the curvature of the surface in the tube.

But, according to views set forth by Poynting,[2] the maximum pressure of a vapor in contact with its liquid at a given temperature is dependent upon the total pressure to which the liquid is subjected; and Poynting attributes the smallness of the pressure above a concave surface to the small pressure borne by the liquid *just beneath* the surface. However sound Poynting's theory, his statement of it at this point lacks clearness; for the fact is apt to stick in the mind of the reader that evaporation and condensation occur, if at all, *at* the curved surface, and that this surface is subjected to the full pressure of the atmosphere; so that the pertinence of referring the state of the vapor to the state of the liquid beneath the surface is not obvious.

Le Blanc,[3] although he does not mention Poynting, maintains an opinion similar to that expressed by the latter, and gives conclusive arguments in favor of it. He refers to an article by Schiller[4] on the same subject.

[1] See Maxwell's Heat.

[2] Phil. Mag., July, 1881, and October, 1896.

[3] Electro-Chemistry, 151, English edition.

[4] Wied. Ann. 53, 396 (1894).

The special algebraic expression obtained below for the relation between temperature, vapor-density, and total pressure, may have been given before, although I do not remember to have seen it; but in any case I hope that the method of its derivation, by following up a commonly neglected term in a familiar operation, will possess a certain interest.

Nernst, *Theoretische Chemie*, p. 510 of the first German edition, derives the "equation of the reaction-isotherms,"

$$K = \frac{c_1'^{n_1'} c_2'^{n_2'} \cdots\cdots\cdots\cdots}{c_1^{n_1} c_2^{n_2} \cdots\cdots\cdots\cdots} = \text{constant},$$

in the following manner: Starting with a mixture in which the reaction occurs according to the scheme,

$$\nu_1 a_1 + \nu_2 a_2 + \cdots + n_1 A_1 + n_2 A_2 + \cdots \rightleftharpoons \nu_1' a_1' + \nu_2' a_2' + \cdots + n_1' A_1' + n_2' A_2' + \cdots,$$

where every a refers to a solid or to a liquid which does not mix with the other substances present and every A to a gaseous or dissolved constituent, every ν to the number of gm. mol. of its a entering into the reaction and every n to the number of gm. mol. of its A entering into the reaction, the whole being contained in a vessel of unchanging volume, Nernst imagines the reaction to go on from left to right with no change whatever in the condition of the reaction mixture, the left-hand constituents being forced in as fast as they are consumed by the reaction and the right-hand constituents forced out as fast as they are produced. The whole operation, being carried on reversibly and isothermally, gives the same amount of work which would be given by any other reversible isothermal process proceeding from the same initial to the same final conditions. Nernst writes this amount of work thus,

$$F = -RT(n_1 ln c_1 + n_2 ln c_2 + \cdots - n_1' ln c_1' - n_2' ln c_2' - \cdots),$$

whence

$$F = RT ln \frac{c_1'^{n_1'} c_2'^{n_2'} \cdots\cdots\cdots}{c_1^{n_1} c_2^{n_2} \cdots\cdots\cdots} = RT ln K, \qquad (1)$$

where each c is the concentration of the corresponding A in the

mixture. Then, as F, however the individual c's may vary, is a constant, K must be a constant; which was the proposition to be proved.

A close examination of the conditions given by Nernst shows, however, that the value of F above given is not, in general, true. The full expression for F is *

$$F = RT/nK - RT(N - N') - P(V - V'), \qquad (2)$$

where

$$N = n_1 + n_2 + \cdots,$$
$$N' = n_1' + n_2' + \cdots,$$

$$V = \text{volume of } \nu_1 a_1 + \nu_2 a_2 + \cdots,$$
$$V' = \quad " \quad " \ \nu_1' a_1' + \nu_2' a_2' + \cdots,$$

P = total pressure per unit surface within the reaction mixture.

In this amended equation, (2), the terms F and RT(N − N′) being constant at constant T, the only impeachment of the conclusion that RT/nK, and so K, is a constant, lies in the variation of the term P(V − V′) with change of P. This change, though usually small, since the whole term P(V − V′) is likely to be small, is unquestionable, and we must conclude that K, as defined by Nernst with reference to the c's only, is not strictly a

*The initial condition of the A constituents outside the reaction vessel, and the final condition of the A′ constituents outside the reaction vessel, is unit concentration, in gas or solution. The reversible, isothermal introduction of n_1 gm. mol. of A_1, for example, into the reaction-vessel involves, first, isothermal expansion from density 1 to density c_1, yielding $-n_1 RT/nc_1$ units of work; second, injection at constant density c_1, through a semipermeable partition, absorbing $n_1 RT$ units of work. The net amount of work obtained from this operation is $-n_1 RT(lnc_1 + 1)$. Similarly, the net amount of work obtained by the ejection of n_1' gm. mol. of A_1' at constant density c_1', and its subsequent compression to density 1, is $n_1' RT(lnc_1' + 1)$. The equation (1), which according to Nernst shows the amount of work accomplished in the whole operation, ignores the fact that Σn, or N, is not necessarily equal to $\Sigma n'$, or N′. We are, however, not concerned with this inaccuracy, which is, by the way, eliminated in Nernst's derivation of the equation for the "*reaction-isochor*." The term P(V′ − V), which appears in (2), obviously gives the net amount of external work obtained from the injection and ejection of the solids or non-miscible liquids which take part in the operation. This amount of work is expressly put aside by Nernst as "*natürlich gleich Null*;" but it is the especial point of the present discussion.

constant at constant T. Let us, therefore, take as the real equilibrium constant

$$C = K \times \frac{k_1'^{\nu_1} k_2'^{\nu_2} \ldots}{k_1^{\nu_1} k_2^{\nu_2} \ldots} = K \times k, \tag{3}$$

where k_x bears the same relation to a_x that c_x bears to A_x, etc.

Substituting now for K in (2), we get

$$F = RT(lnC - lnk) - RT(N - N') - P(V - V'). \tag{4}$$

At constant temperature the only variable terms in this equation are $RTlnk$ and $P(V - V')$. Hence at constant temperature

$$RTlnk + P(V - V') = B, \tag{5}$$

where B is a constant as regards P.

From (5) we get

$$k = \epsilon^{\frac{P(V'-V)+B}{RT}}, \text{ or } \frac{k_1^{\nu_1} k_2^{\nu_2} \ldots}{k_1'^{\nu_1} k_2'^{\nu_2} \ldots} = \epsilon^{\frac{P(V-V')-B}{RT}}, \tag{6}$$

where ϵ is the Napierian base.

Let us apply equation (6) to the case of a single liquid or solid in the presence of a gaseous phase consisting of the saturated vapor of this liquid or solid together with any number of other gases neutral to the first substance, the condensed phase of this substance being forced into an inclosure as fast, by weight, as its vapor is withdrawn, the "reaction" being simply evaporation. In this case $V' = 0$, $\nu_1 = 1$, and, if v_1 is the volume of 1 gm. mol. of the substance in the condensed phase, we get from (6)

$$k_1 = \epsilon^{\frac{Pv_1 - B}{RT}}, \quad \text{or } k_1 = \epsilon^{\frac{Pv_1}{RT}} \times \epsilon^{\frac{b}{RT}}, \tag{7}$$

where $b = -B$.

It will be remembered that B, and so b, is independent of P. Hence the last equation may be written

$$k_1 = \epsilon^{\frac{Pv_1}{RT}} \times \epsilon^{f(T)}, \tag{8}$$

$f(T)$ being some function of T.

Taking, for example, ice at $-10°$ C as the condensed phase,

and reckoning in atmospheres and liters, we get for the vapor-density of water over the ice

$$k_1 = \epsilon^{\frac{P}{1100}} \times \epsilon^{f(T)} \qquad (9)$$

when P is very small, $\epsilon^{\frac{P}{1100}}$ = approximately 1

" " 1 atmos, " = " 1.0009,
" " 2 " " = " 1.0018,
" " 100 " " = " 1.0950.

In the presence of liquid water at 0° C, we should have $k_1 = \epsilon^{\frac{P}{1240}} \times \epsilon^{f(T)}$, where $f(T)$ is not the same as in equation (9). In this case

when P is very small $\epsilon^{\frac{P}{1240}}$ = approximately 1

" " 1 atmos, " = " 1.0008,
" " 2 " " = " 1.0016,
" " 100 " " = " 1.0840.

Of course, the same results can be found without any reference to the general "equation of the reaction-isotherm."

Cambridge, June 1, 1899.

THE ELECTRICAL CONDUCTIVITY OF NON-AQUEOUS SOLUTIONS[1]

BY AZARIAH T. LINCOLN

A preliminary report on the electrical conductivity of non-aqueous solutions by Professor Kahlenberg and myself has appeared in an article entitled "The Dissociation Power of Solvents."[2] I have since been engaged in investigating the subject further, and desire in this present article to present the experimental results that I have obtained and also to inquire what the bearing of these facts is upon the theory of electrolytic dissociation as promulgated by Arrhenius, and to determine to what extent this theory can be applied to non-aqueous solutions. In view of the fact that Arrhenius' theory is not accepted by a large number of chemists to-day, and in the face of the data that have been collected, one may well hesitate to apply this theory to non-aqueous solutions until there is a sufficiently firm experimental basis to justify it. Auxiliary theories have been promulgated to explain the facts presented by numerous investigators, and an attempt will be made to show to what extent these theories are compatible with the experimental results herein presented.

In an investigation of the electrical conductivity of non-aqueous solutions, the chief requirement is that both the solvents and the dissolved substances be absolutely free from water. To accomplish this is not an easy task. Then, too, the question arises as to what anhydrous salts are soluble in the various solvents. In many cases this could only be answered by experi-

[1] From the author's thesis for the degree of Doctor of Philosophy, presented to the faculty of the University of Wisconsin, June, 1899. Published in full in the Transactions of the Wisconsin Academy of Sciences, Arts, and Letters, Vol. XII, pp. 395–453.

[2] Jour. Phys. Chem. 3, 12 (1899).

ment. The qualitative results previously published were confined to ferric chloride, antimony trichloride, bismuth trichloride and mercuric chloride. In addition to these, salts of other heavy metals have been employed in this investigation. Even when these salts were readily soluble, conducting solutions were not always obtained. In order to determine what solutions conduct and to estimate roughly at least the relative magnitude of the conductivity, it was necessary to perform an elaborate series of qualitative experiments to ascertain what solvents yield solutions having a conductivity sufficient to justify quantitative measurements.

The method employed in making these tests has been previously described. The solvents were all of the C. P. variety of standard makes. The salts employed were absolutely anhydrous and the method employed in their preparation and dehydration will now be given. The preparation of cupric chloride, mercuric chloride, stannous and aluminium chlorides, stannic chloride, arsenic trichloride, and the trichloride of phosphorus has been previously described. A C. P. sample of lithium chloride from Merck was dehydrated for several days at a temperature not to exceed 120°. It was then removed to a mortar, thoroughly pulverized and then replaced in the air-bath for about a day longer. The following salts were recrystallized several times and then dehydrated in the manner just described: manganous chloride from Merck, chlorides of nickel and cadmium from Schuchardt, and cobaltic chloride from Trommsdorff. The C. P. samples of lead nitrate and mercuric iodide from Merck, mercuric cyanide from Trommsdorff, and zinc chloride from Kahlbaum, were dehydrated in the manner similar to that just described. The silver cyanide was prepared from potassium cyanide and silver nitrate by Professor Kahlenberg, who dehydrated it and upon subsequent analysis found it to be pure.

Since the qualitative determinations throw some light upon the dissociative power of the solvents, the following additional results are given in Table I. In the first two columns are given

the names and formulæ of the solvents. In the next eighteen columns is indicated whether the solutions of the salts whose formulæ head the respective columns, conduct electricity. When the solution conducted so poorly that no deflection of the galvanometer needle was observed, the fact is indicated by the minus sign (—). The plus sign (+) indicates that the solution did conduct. The addition of the interrogative sign to the plus sign (+?) indicates that a very slight movement of the needle was detected; and when the plus sign is followed by the exclamation mark (+!), this indicates that the solution conducts sufficiently well to make a qualitative determination desirable. Blank spaces indicate that determinations were not made, and the letter i indicates that the salt was insoluble in the solvent or very difficultly soluble. In the last two columns respectively are given the dielectric constants and the coefficients of association of the solvents. The data in these two columns are as complete as could be obtained from the literature.[1] The letters R and S refer to the article by Ramsay and Shields[2] as authority, R and A to the work of Ramsay and Aston,[3] and D and F to that of Dutoit and Friderich.[4] The letter V designates determinations by Vollmer, C by Carrara, and S by Schlamp.

As many quantitative determinations of the conductivity of alcoholic[5] solutions have been made, it was unnecessary to make

[1] Thwing. Zeit. phys. Chem. **14,** 286 (1894). Drude. Zeit. phys. Chem. **23,** 308 (1897).

[2] Jour. Chem. Soc. **63,** 1089 (1893).

[3] Ibid. **65,** 168 (1894).

[4] Bull. Chim. Soc. Paris, (3) **19,** 321 (1898).

[5] (1) Carrara. Gazz. Chim. Ital. **24,** II, 504. (Ref.) Jour. Chem. Soc. **68,** ii, 302 (1895); Ibid. **26,** I, 119. (Ref.) Jour. Chem. Soc. **70,** ii, 511 (1896); Ibid. **27,** I, 422. (Ref.) Jour. Chem. Soc. **72,** ii, 473 (1897). (2) Cattaneo. Rend. Accad. Linc. (5) **4,** II, 63, 73 (1895). (Ref.) Jour. Chem. Soc. **72,** ii, 537 (1897). (3) Cohen. Zeit. phys. Chem. **25,** 1 (1898). (4) Fitzpatrick. Phil. Mag. (5) **24,** 322 (1887). (5) Holland. Wied. Ann. **50,** 261 (1893). (6) Kablukoff. J. Russ. Chem. Soc. **23,** 391. (Ref.) Jour. Chem. Soc. **64,** ii, 151 (1893). (7) Pfeiffer. Wied. Ann. **26,** 31 (1885). (8) Schall. Zeit. phys. Chem. **14,** 701 (1894). (9) Schlamp. Zeit. phys. Chem. **14,** 273 (1894). (10) Vollmer. Wied. Ann. **52,** 328 (1894). (11) Zelinsky and Krapiwin. Zeit. phys. Chem. **21,** 35 (1896).

TABLE I

Solvent	Formula	$AlCl_3$	$CrCl_2$	$MnCl_2$	$ZnCl_2$	$CoCl_2$	$NiCl_2$
Methyl alcohol	CH_3OH						
Ethyl alcohol	C_2H_5OH						
Propyl alcohol	$CH_3(CH_2)_2OH$						
Allyl alcohol	C_3H_5OH						
Benzyl alcohol	$C_6H_5CH_2OH$	i	—		—		
Benzaldehyde	$C_6H_5.COH$						
Salicylic aldehyde	$C_6H_4CHO.OH$	—		—	i	i	—
Furfurol	$C_5H_4O_2$			i	+	—	—
Acetone	$(CH_3)_2CO$						
Methyl-propyl ketone	$CH_3C_3H_7.CO$	+			+	—	
Acetophenone	$CH_3COC_6H_5$	+		i	+	—	i
Ethyl acetate	$CH_3COOC_2H_5$						
Ethyl monochloracetate	$CH_2ClCOOC_2H_5$	—		i	+	—	i
Ethyl cyanacetate	$CH_2CN.COOC_2H_5$	+		i	+ (?)	—	i
Ethyl acetoacetate	$CH_3CO.CH_2COOC_2H_5$			i	+	+	i
Ethyl benzoate	$C_6H_5COOC_2H_5$		i		+ (?)		
Ethyl oxalate	$(COO.C_2H_5)_2$		—	i	+	—	i
Ethyl nitrate	$C_2H_5NO_3$	+	i	i	i	i	i
Amyl nitrite	$C_5H_{11}NO_2$			i	+ (?)	—	i
Nitrobenzene	$C_6H_5NO_2$	+	i		i		
o-Nitrotoluene	$C_6H_4.CH_3NO_2$			i		i	i
Aniline	$C_6H_5NH_2$						
Xylidine (meta asym.)	$C_6H_3(CH_3)_2.NH_2$						
Benzonitrile	C_6H_5CN						
Pyridine	C_5H_5N	+	+	i	+	+	i
Piperidine	$C_5H_{11}N$			—	—	—	—
Quinoline	C_9H_7N			i	+	—	—
Phosphorus trichloride	PCl_3						
Tin tetrachloride	$SnCl_4$						

TABLE I—(*Continued*)

$CuSO_4$	$CuCl_2$	$CdCl_2$	$AsCl_3$	$SnCl_2$	$Pb(NO_3)_2$	$Hg(CN)_2$	HgI_2	$AgNO_3$	AgCN	KCl	LiCl	Dielectric constant (Air = 1)	Coefficient of association
											V	32.65 Teres'n	3.43 R and S
	+!	i						V			V	25.7 Rosa	2.74 R and S
											S	20.8 Thwing	2.25 R and S
								+!			+!	21.6 "	1.88 R and S
	—							—			+!	10.6 Drude	
								i				14.48 Thwing	0.97 R and S
	—	—			i	i	—	i			+!	19.21 "	
i		i			—		+	+			+!	39.4 Drude	
	+!			+							C	21.85 Thwing	1.26 R and S
	+						+	i			i	16.75 "	1.11 R and S
i	i	i			i	—	—	—			+(?)	16.4 "	1.10 R and S
	+			+								6.5 Teresh'n	0.99 R and S
—	+	i			i	i	—	—		i	+(?)		
i	+!	i			i	—	—	+!		i	i	26.7 Drude	
	+		+		i		—	i			+!	15.7 "	0.96 R and S
	i							i			i	6.5 Teresh'n	
i	—	i			i	—	—	i			+(?)		
	i	i			i	i	i				i	17.72 Thwing	
i	i	i			i	i	—	i		i	—		
	i		+					i		i		32.19 "	{0.93 / 1.13} R and S
i	+(?)	i			i		—	i			i	26.58 "	
								+!				{7.5 Teres'n / 7.15 Drude}	1.05 R and S
								+!					
								+!				26.0 Drude	{0.97 R and S / 1.00 Traube}
i	+	i			+	+	+	+!	+		+!		0.93 R and S
—		i			i		—	+			—		1.08 R and S
+		i			i		—	+			—		0.81 R and S
						i				i			1.02 R and S
			i							i			

qualitative tests in this connection. Solutions of lithium chloride in salicylic aldehyde conducts very well. The specific inductive capacity of furfurol would indicate that this solvent would yield solutions that conduct; and such is the case. The dissociative power of the solvents has been previously considered and consequently there are but few additions to be made to what has already been given. Silver nitrate is quite soluble in aniline and xylidine and both yield solutions that conduct very well. A large number of other tests were made which were too detailed to be included in these tabulated results. Suffice it to say, however, that of the very large number of tests made both of organic and inorganic substances in these numerous solvents, there was not one instance when the solution conducted electricity, in which the dissolved substance was not an acid, a base, or a salt.

The additional results of the quantitative measurements of the electrical conductivity will now be given. A resistance cell of the Arrhenius pattern with the electrodes about three millimeters apart was used in making these determinations. The usual method of making the dilutions could not be employed owing to the small quantity of the solvents available. Into the resistance cell was introduced ten cc of the solvent by means of a carefully calibrated burette. The conductivity was measured and then a weighed portion of the salt was introduced, and when this was all in solution the conductivity was measured. Portions of the salt were successively introduced and the conductivity measurements made, until the requisite number of dilutions were made.

In the following tables v represents the volume in liters in which one gram-molecule was contained and μ the molecular conductivity expressed in reciprocal mercury units. The measurements were made at 25° unless otherwise specified. The higher temperatures were obtained by heating the cell with its contents in a paraffin bath and the conductivity was measured as the temperature increased.

ALLYL ALCOHOL

A C. P. sample of allyl alcohol from Merck was treated with

poatssium carbonate, over which it stood for several days. From this it was distilled and the distillate treated with fused potassium hydroxide. The distillate from this was treated with caustic potash in contact with which it stood several days and it was then distilled. This distillate was redistilled twice and the conductivity determinations made as soon as possible. The specific conductivity was 6.5×10^{-6}.

TABLE II

Solvent: allyl alcohol

Ferric Chloride, $FeCl_3$		Ferric Chloride, ($v = 20.02$ at 25°)	
v	μ	t	μ
20.02	17.42	25°	17.42
53.71	23.03	50	34.62
115.60	32.15	73	43.63
		80	45.65

BENZYL ALCOHOL

The sample of benzyl alcohol employed was from Merck and was rectified by distillation. The portion used had a very constant boiling-point. Owing to the difficult solubility of the salts and the slight conductivity of solutions of this solvent, very few determinations were made. The specific conductivity was 1.76×10^{-6}.

TABLE III

Solvent: benzyl alcohol

Ferric Chloride, $FeCl_3$		Ferric Chloride, ($v = 88.06$ at 25°)	
v	μ	t	μ
88.06	2.62	25°	2.62
895.22	6.31	54	5.08
		85	6.46
		100	7.19

PARALDEHYDE

The sample of paraldehyde from Kahlbaum was distilled and the portion coming over at a very constant temperature was employed. The specific conductivity was less than 3.4×10^{-7}.

TABLE IV

Solvent: paraldehyde

Ferric Chloride, $FeCl_3$		Antimony Trichloride, $SbCl_3$		Antimony Trichloride, ($v = 5.57$ at 25°)	
v	μ	v	μ	t	μ
4.37	9.81	5.57	0.202	25.2°	0.295
21.32	16.91	20.76	0.356	26.6	0.299
42.52	18.76	61.16	0.532	29.0	0.298
81.88	19.16			32.0	0.295
183.11	16.51				
575.50	16.91				

SALICYLIC ALDEHYDE

The sample of salicylic aldehyde from Schuchardt was rectified by distillation. The portion taken had a constant boiling-point and the specific conductivity was 5.98×10^{-6}.

TABLE V

Solvent: salicylic aldehyde

Ferric Chloride,[1] $FeCl_3$		Ferric Chloride, ($v = 20.39$ at 25°)	
v	μ	t	μ
20.39	3.76	25°	3.76
81.38	4.71	45	6.30
220.74	5.60	50	6.73
		109	6.46

FURFUROL

The sample of furfurol from Merck was treated with fused calcium chloride, over which it stood for several weeks. It was then distilled and the distillate again distilled. The portion coming over between 156° and 158° at 744 mm pressure was collected and its specific conductivity was 2.4×10^{-5}.

TABLE VI

Solvent: furfurol

Ferric Chloride, $FeCl_3$		Ferric Chloride, ($v = 45.60$ at 25°)		Ferric Chloride, ($v = 45.60$ at 25°)	
v	μ	t	μ	t	μ
45.60	20.78	25°	20.78	75°	47.96
80.98	22.20	45	37.83	85	51.41
149.21	26.42	55	40.98	95	56.07
		65	44.06	105	60.02

[1] Apparently this did not quite all dissolve. After cooling it became a viscous mass.

METHYL-PROPYL KETONE

The sample of methyl-propyl ketone employed was from Schuchardt and gave a specific conductivity of 9.5×10^{-7}.

TABLE VII

Solvent : methyl-propyl ketone

Ferric Chloride, $FeCl_3$		Ferric Chloride, $FeCl_3$		Ferric Chloride, ($v = 13.64$ at 25°)		Ferric Chloride, ($v = 13.64$ at 25°)	
v	μ	v	μ	t	μ	t	μ
13.64	28.25	111.13	41.59	25°	28.25	60°	34.07
22.83	31.07	164.43	46.15	49	33.47	70	35.60
53.36	36.98	358.09	50.28	50	33.66	75	35.89
100.71	42.76	1074.27	59.52	55	33.79	80	36.17

$CuCl_2$ in less than 460.28 liters gave $\lambda = 5.22 \times 10^{-6}$. A resistance of 6000 ohms was introduced in the measuring.

ACETOPHENONE

A sample of acetophenone from Schuchardt was treated with barium oxide, over which it stood for several days, and then distilled. The distillate was redistilled and the portion coming over between 194° and 195° at 745 mm pressure was taken. The specific conductivity of this portion was 1.8×10^{-7}.

TABLE VIII

Solvent : acetophenone

Ferric Chloride, $FeCl_3$		Ferric Chloride, ($v = 23.46$ at 25°)		Ferric Chloride, ($v = 23.46$ at 25°)	
v	μ	t	μ	t	μ
23.46	10.28	25°	10.28	114°	27.49
46.71	11.03	50	15.17	125	28.74
65.77	11.59	65	17.52	135	28.85
124.91	12.03	80	20.52	150	28.16
292.98	13.08	100	23.90		

ETHYL MONOCHLORACETATE

This solvent was a C. P. sample from Schuchardt, the boiling-point of which was 143.5°. The specific conductivity was less than 1.7×10^{-6}.

TABLE IX

Solvent: ethyl monochloracetate

Ferric Chloride, $FeCl_3$		Ferric Chloride, ($v = 7.76$ at 25°)		Antimony Trichloride, $SbCl_3$	
v	μ	t	μ	v	μ
7.76	12.45	25°	12.45	4.25	0.174
14.96	13.14	50	15.21	11.49	0.201
19.18	13.49	55	15.77	44.73	0.337
22.09	13.75	67	16.28	Cupric Chloride, $CuCl_2$	
45.63	14.78	80	16.28	v	μ
92.05	16.38	92	15.61	13.32	1.24
152.55	17.88	100	14.73		
		110	13.11		

The $CuCl_2$ did not quite all dissolve; so $\lambda = 1.33 \times 10^{-5}$.

ETHYL CYANACETATE

This solvent was a C. P. sample from Schuchardt and was rectified by redistillation. The boiling-point was very constant, and the portion collected came over between 203° and 203.5° at 744 mm pressure. The specific conductivity was 3.7×10^{-7}.

TABLE X

Solvent: ethyl cyanacetate

Silver Nitrate, $AgNO_3$		Ferric Chloride, $FeCl_3$		Ferric Chloride, ($v = 15.30$ at 25°)		Cupric Chloride, $CuCl_2$	
v	μ	v	μ	t	μ	v	μ
10.62	4.19	15.30	8.88	25°	8.88	29.85	7.00
19.00	4.78	19.72	8.99	49	13.40	41.67	7.50
28.30	5.29	27.08	9.29	60	15.85	59.40	8.08
58.57	6.46	44.64	9.80	75	20.14	97.77	12.80
110.97	7.66	185.22	11.57	87	22.44		
				100	24.83		
				125	29.49		
				150	38.70		

ETHYL OXALATE

This solvent was a C. P. sample from Merck, and its specific conductivity was 7.12×10^{-7}.

TABLE XI

Solvent: ethyl oxalate

Ferric Chloride, $FeCl_3$		Ferric Chloride, $FeCl_3$		Ferric Chloride, ($v = 13.15$ at 25°)		Ferric Chloride, ($v = 13.15$ at 25°)	
v	μ	v	μ	t	μ	t	μ
13.15	5.88	94.79	6.25	25°	5.88	75°	10.15
22.07	5.89	342.85	7.70	50	8.11	100	11.14
42.29	5.92			62	9.21	125	9.58

(At 148° solution began to boil.)

ETHYL BENZOATE

This sample was a C. P. sample from Trommsdorff, and its specific conductivity was about 1.8×10^{-7}.

TABLE XII

Solvent: ethyl benzoate

Ferric Chloride, $FeCl_3$		Ferric Chloride, ($v = 29.54$ at 25°)	
v	μ	t	μ
29.54	1.55	25°	1.55
174.28	1.61	56	1.16
517.21	1.91	75	0.82
		100	0.48

AMYL NITRITE

This solvent was a C. P. sample from Schuchardt, and its specific conductivity was 1.8×10^{-7}.

TABLE XIII

Solvent: amyl nitrite

Ferric Chloride, $FeCl_3$		Ferric Chloride, $FeCl_3$		Ferric Chloride, ($v = 21.34$ at 25°)	
v	μ	v	μ	t	μ
21.34	1.54	104.64	2.29	25°	1.54
29.03	1.63	264.16	3.00	50	1.13
38.74	1.74	644.56	3.73	55	1.08
69.46	2.02			64	1.21

(At about 70° the solution began to boil.)

NITROBENZENE

The sample of nitrobenzene employed was from Kahlbaum and was prepared from crystallizable benzene. The specific conductivity was less than 3.5×10^{-7}.

TABLE XIV

Solvent : nitrobenzene

Bismuth Trichloride, $BiCl_3$		Bismuth Trichloride, $BiCl_3$		Aluminium Chloride, $AlCl_3$[1]	
v	μ	v	μ	v	μ
8.50	0.80	68.04	1.03	4.69	3.67
17.01	0.91	136.07	1.07	9.38	4.51
34.02	0.96	272.14	1.11		

ORTHO NITROTOLUENE

The C. P. sample of this solvent employed was from Kahlbaum, and the specific conductivity was less than 1.8×10^{-7}.

TABLE XV

Solvent : ortho nitrotoluene

Ferric Chloride, $FeCl_3$		Ferric Chloride,[2] ($v = 10.91$ at 25°)		Antimony Trichloride, $SbCl_3$	
v	μ	t	μ	v	μ
10.94	8.37	25°	9.39	3.40	0.056
16.38	9.44	46	11.98	6.55	0.088
25.99	10.74	60	12.77	19.82	0.244
74.28	13.32	70	12.92	34.10	0.389
201.43	15.24	80	12.67	Mercuric Chloride, $HgCl_2$	
		90	12.12	v	μ
		100	11.46	105.43	0.628

META NITROTOLUENE

The C. P. sample of this solvent was from Kahlbaum, and the specific conductivity was less than 1.8×10^{-7}.

TABLE XVI

Solvent: meta nitrotoluene

Ferric Chloride, $FeCl_3$		Ferric Chloride, ($v = 10.86$ at 25°)		Ferric Chloride, ($v = 10.86$ at 25°)	
v	μ	t	μ	t	μ
10.86	6.86	25°	6.86	80	15.66
46.93	11.10	50	12.28	90	17.35
84.77	12.55	60	13.05	100	18.20
448.14	19.00	70	13.82	125	16.80
814.81	18.20				

[1] Aluminium chloride dissolved with evolution of heat. When the solution was diluted the evolution of hydrochloric acid gas was very perceptible, and for this reason no further determinations were made.

[2] This solution remained in the resistance cell for two hours before the determinations were made.

BENZONITRILE

The C. P. sample of this solvent employed was from Trommsdorff, and the specific conductivity was 1.9×10^{-6}.

TABLE XVII

Solvent: benzonitrile

Silver Nitrate, $AgNO_3$		Silver Nitrate, $AgNO_3$		Silver Nitrate, ($v = 2.09$ at 25°)		Silver Nitrate, ($v = 2.09$ at 25°)	
v	μ	v	μ	t	μ	t	μ
2.09	3.37	58.98	11.19	25°	5.55(?)	95°	9.26
9.43	5.18	83.92	13.41	50	6.75	105	9.65
16.33	6.37	151.96	16.38	56	7.05	114	10.09
24.06	7.66	301.21	18.20	65	7.59	125	10.69
44.62	10.12	803.24	21.64	77	8.11	135	11.20
				87	8.75	150	11.70

PYRIDINE

The sample of pyridine from König was fractionated, and the portion distilling over between 106° and 117° was treated with fused caustic potash from which it was distilled. The distillate was again treated with caustic potash, over which it stood for several days and was then distilled. The distillate was redistilled and the portion coming over between 113° and 114° at 742 mm pressure was employed in some of the following determinations. The specific conductivity was 7.6×10^{-7}. For other determinations a C. P. sample of the solvent from Kahlbaum was employed, and its specific conductivity was about 7.5×10^{-7}.

TABLE XVIII

Solvent: pyridine

Ferric Chloride, $FeCl_3$		Ferric Chloride, λ of solvent $= 1.74 \times 10^{-6}$.		Ferric Chloride, ($v = 6.06$ at 25°)		Ferric Chloride, ($v = 6.06$ at 25°)	
v	μ	v	μ	t	μ	t	μ
(First Series)		(Second Series)		25°	7.96	80°	21.16
6.06	7.96	45.52	6.32	54	16.50	85	22.71
15.02	7.52	93.69	5.91	59	17.24	90	23.36
24.56	6.85	159.55	5.57	65	18.23	95	24.12
42.18	6.82			70	19.59	100	24.80
95.35	6.41			75	20.40	105	25.61
						110	25.61

Silver Nitrate, $AgNO_3$		Silver Nitrate, $AgNO_3$		Lead Nitrate, $Pb(NO_3)_2$		Mercuric Iodide, HgI_2	
v	μ	v	μ	v	μ	v	μ
First Series		Second Series		21.10	0.81	21.78	0.35
7.55	24.07	392.28	40.16	55.96	1.57	93.61	1.39
10.71	24.87	588.42	43.13	168.47	3.25	200.12	2.70
17.70	25.79	784.56	45.21	Cupric Chloride, $CuCl_2$		Silver Tartrate, $C_6H_4O_6Ag_2$	
25.52	26.91	Silver Cyanide, AgCN		v	μ	v	μ
27.43	27.29	v	μ	45.10	0.98	340.74	14.64
37.32	27.96	14.64	4.78	57.04	1.16	505.91	35.29
51.43	29.49	24.52	5.04	Mercuric Cyanide, $Hg(CN)_2$		Cobaltic Chloride, $CoCl_2$	
60.90	30.17	38.40	5.42	v	μ	v	μ
93.71	30.83	100.47	6.16	5.35	0.012	74.06	0.20
140.57	36.21	393.01	6.47	13.09	0.014	805.31	1.45
				357.42	0.153		

A solution of cobaltic chloride becomes deep blue at a temperature between 40° and 50°. The following specific conductivity determinations were made in order to ascertain whether the two differently colored solutions had the same conductivity.

	λ at 25°	λ at 55°
Solvent	7.5×10^{-7}	1.4×10^{-6}
Saturated solution of $CoCl_2$ at 25°	2.9×10^{-6}	5.5×10^{-6}

PIPERIDINE

A C. P. sample of this solvent from Kahlbaum was employed, and its specific conductivity was less than 1.8×10^{-7}.

TABLE XIX

Solvent: piperidine

Silver Nitrate, $AgNO_3$		Silver Nitrate, $AgNO_3$		Silver Nitrate, ($v = 4.24$ at 25°)		Silver Nitrate, ($v = 4.24$ at 25°)	
v	μ	v	μ	t	μ	t	μ
4.24	0.368	10.50	0.091	25°	0.368	40°	0.453
5.25	0.277	15.62	0.043	30.5	0.391	45	0.478
7.88	0.154			35	0.432	50	0.508

QUINOLINE

The sample of this solvent employed was from Merck, and its specific conductivity was 3.7×10^{-7}.

TABLE XX

Solvent : quinoline

Silver Nitrate, $AgNO_3$		Silver Nitrate, ($v = 4.80$ at 25°)		Silver Nitrate, ($v = 4.80$ at 25°)	
v	μ	t	μ	t	μ
4.80	2.45	25°	2.45	85°	5.89
9.60	2.79	50	4.67	104.	5.75
34.92	2.80	62	5.20	124	5.77
129.83	3.62	70	5.52	136	5.52

Limiting values for the molecular conductivity can be obtained in aqueous solutions, but this is, however, generally not the case in non-aqueous solutions. A few examples of those solvents that yield solutions that conduct the best will be given to illustrate this.

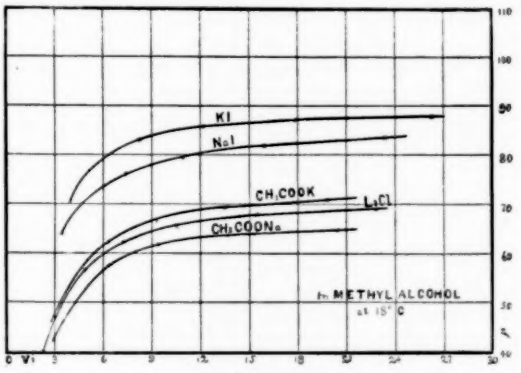

Fig. 1

In Fig. 1 is plotted the molecular conductivity of various salts in methyl alcohol from the determinations of Vollmer at 18°. The molecular conductivity is represented by the ordinates and the cube root of the volume in which one gram-molecule of the substance was dissolved by the abscissas. The cube root of the volume was employed in order to represent the values for the more dilute solutions in the figure. In Fig. 2 are plotted the results of Zelinsky and Krapiwin determined at 25°. In most cases, it will be observed that limiting values are

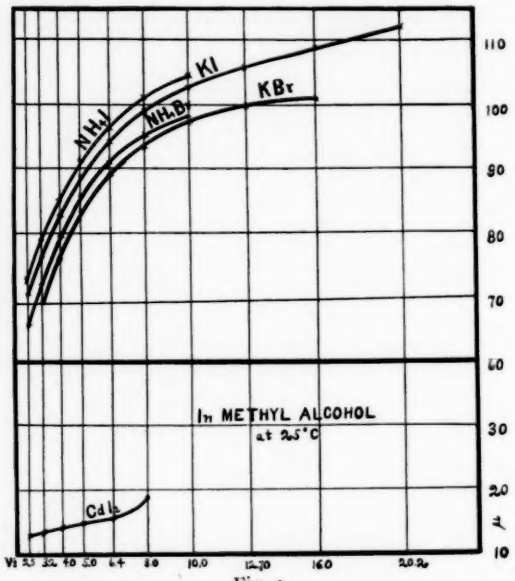

Fig. 2

reached, CdI_2 being, however, an exception, Zelinsky's and Krapiwin's determinations for KI indicate that the curve would probably not become asymptotic and, therefore, no limiting value for μ would be reached. Nevertheless, Carrara assigns 97 as the value for μ_∞. Cohen has pointed out that the difference in the determinations of Zelinsky and Krapiwin and of Carrara may be attributed to the effects of the alcohol on the platinum black electrodes which they employ. In Fig. 3 is plotted the molecular conductivity of various salts in ethyl alcoholic solutions from the determinations of Vollmer at 18°. It will be noticed that the salts of the alkalies yield limiting values for μ, while in the case of $CaCl_2$ there seems to be no tendency for the curve to become asymptotic. The same is true for $Ca(NO_3)_2$, and according to my determinations for $FeCl_3$ and $SbCl_3$.

Carrara has calculated the values of μ_∞ for a number of halogen salts from Campetti's[1] determinations of the transfer-

[1] Nuovo Cimento [3] **35**, 225. (Ref.) Jahr. der Elektrochemie, **1**, 22 (1894).

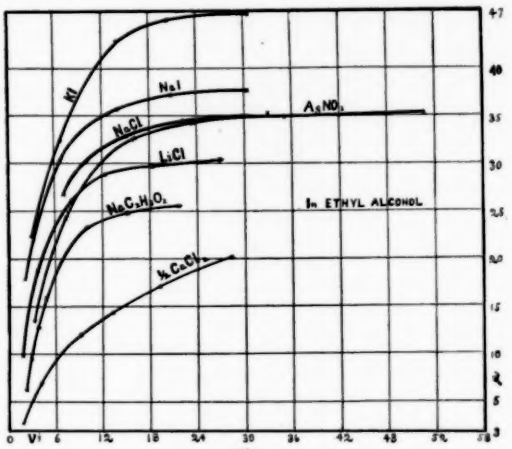

Fig. 3

ence figures of the halogens in methylic alcohol solutions. He finds these values to agree very closely with his own experimental results. In the following table are given these results and also the value of μ_∞ in water.

TABLE XXI

Values of μ_∞

	In Methyl Alcohol			
	Cl	Br	I	OH
H	133.80	....	134.50	....
Li	77.30	....	....	....
Na	86.80	87.58	89.77	71.83
K	95.57	96.52	97.63	75.75
NH_4	96.24	99.93	105.25	82.00
$N(CH_3)_4$	....	....	115.30	....
$N(C_2H_5)_4$	95.76	96.62	113.76	91.13
$S(CH_3)_3$	100.09	102.50	116.38	97.34
	In Water			
	Cl	Br	I	OH
H	395.20	398.0	397.0	....
Li	110.00	....	....	....
Na	119.40	122.2	121.4	216.2
K	140.80	143.6	142.6	237.6
NH_4	140.6	143.4	142.6	230.0
$N(CH_3)_4$	....	....	115.6	....
$N(C_2H_5)_4$	102.4	105.2	104.2	199.2
$S(CH_3)_3$	117.8	120.3	119.3	214.0

From Campetti's results Carrara calculated the rate of migration of the ions in methyl alcoholic solutions and the results are given in the following table, which is taken from the *Jahrbuch der Elektrochemie*, **3**, 13 (1896).

TABLE XXII

Speed of Migration

	In Methyl Alcohol			In Water
	Cl	Br	I	
Li	27.83	....	....	39.8
Na	37.33	37.33	37.33	49.2
K	46.10	46.26	45.19	70.6
NH_4	46.77	49.49	53.81	70.4
$N(CH_3)_4$	....	....	63.08	43.6
$N(C_2H_5)_4$	46.29	46.36	61.34	32.2
$S(CH_3)_3$	51.43	49.85	63.94	47.6
H	85.53	....	82.50	325.0
OH		32.00		170.0
Cl		49.47		70.2
Br		50.24		73.0
I		52.44		72.0
CH_3COO		32.99		38.4
CCl_3COO		35.95		32.8

Kawalki[1] found that the diffusion coefficient of a number of substances in ethyl alcohol is 0.34 times as great as in water. Vollmer from his work observed that the conductivity in ethyl alcoholic solutions at 18° is approximately 0.34 times as great as in aqueous solutions, while his empirical factor for methyl alcohol is 0.73. In general limiting values can be obtained for μ in methyl and ethyl alcoholic solutions except in the case of some salts of the heavy metals.

In other alcoholic solutions no such uniformity seems to exist. This is perhaps best illustrated in the case of solutions in propyl alcohol. The molecular conductivity of solutions in this solvent is represented in Fig. 4. The determinations are from Schlamp's[2] work. It will be noted that lithium salicylate is the only salt the conductivity of which appears to approach a

[1] Wied. Ann. **52**, 300 (1894).

[2] Zeit. phys. Chem. **14**, 272 (1894).

limiting value. Schlamp does not hesitate, however, to assign values for μ_∞ in all cases, and from the plotted results this seems hardly justifiable. In the case of other alcoholic solutions, the

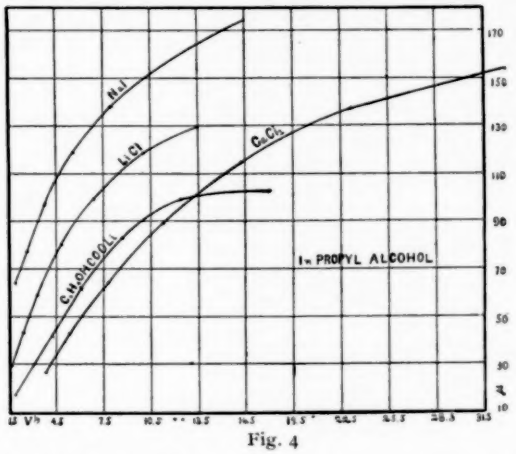

Fig. 4

experimental evidence is so meagre that no generalization can be made (See Tables II, III).

The ketones were found to yield solutions that conduct electricity and this is in keeping with what the other investigators[1] have found.

Acetone yields solutions the conductivity of which is, in general, better than in the case of many of the other ketones. In Fig. 5 is represented the conductivity of a number of salts in this solvent. The results plotted are from the determinations of Carrara principally, while those designated L are from Laszczynski, and those with D from Dutoit and Aston.

It will be noted that very few salts yield solutions in acetone that have limiting values for μ. The values for two curves, for NaI and for $N(C_2H_5)_4I$, appear to indicate a decrease in the conductivity after certain dilutions are reached. The two curves

[1] (1) Laszczynski. Zeit. Elektrochemie, **2**, 55 (1895). (2) Carrara. Gazz. Chim. Ital. **27**, I, 207. (Ref.) Jahr. der Elektrochemie, **4**, 48 (1897). (3) Dutoit and Aston. Comptes rendus, **125**, 240 (1897).

plotted for KI apparently intersect at about $\mu = 153$. Laszczynski thinks the value of μ_∞ lies between 160 and 170. Assuming the former value he calculates the factor k in the formula $\mu_\infty = k(\mu + v)$ where $(\mu + v)$ is the conductivity at infinite dilution in water and k is a constant. The value of k he finds to be 1.3. If this method be applied to salts other than the one he

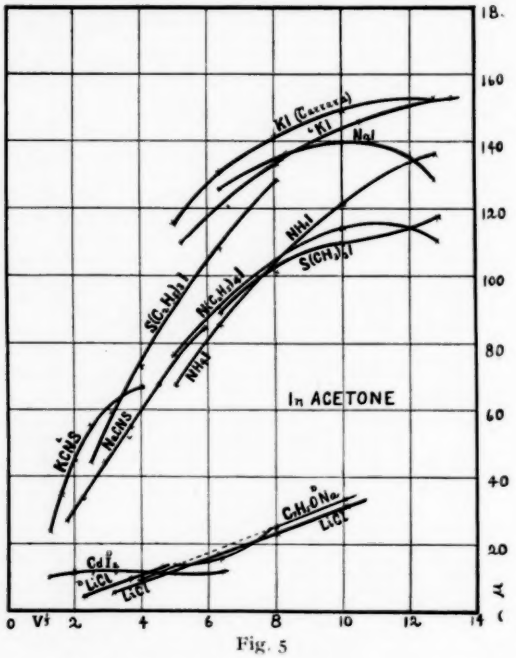

Fig. 5

employed, KI, — to CdI_2 for instance, — it will be found that different values for k will be obtained. There is no such agreement between the limiting values for μ in acetone and in water as Vollmer found to hold in the case of ethyl alcohol and water.

In the other ketones the conductivity is not as great as in acetone, and while limiting values are obtained in some cases, they are of the same order as CdI_2 in acetone, that is, the value

of μ remains virtually constant with the dilution. So in general limiting values in the ketones cannot be obtained.

Laszczynski and Gorski[1] have measured the molecular conductivity of a number of salts in pyridine and their results are plotted in Fig. 6. They assign limiting values to μ in the case

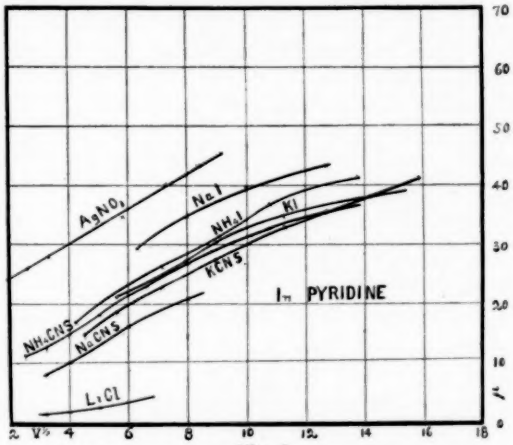

Fig. 6

of NH_4CNS, NH_4I, KI, and NaI. It appears that the curves representing the conductivity of the solutions of these salts might become asymptotic. The values for $AgNO_3$ are my own determinations and these do not appear to approximate to a limiting value for μ, at least not in the dilutions at which the measurements were made. The conductivity of the other salts in pyridine is rather low and limiting values cannot, in general, be obtained.

Silver nitrate in benzonitrile does not yield limiting values for μ. The solutions in the other nitriles conduct well, but they do not generally yield limiting values for μ. Ferric chloride in nitrobenzene yields solutions in which the value of μ approaches a limit.

From the preceding it appears that there is no general uni-

[1] Zeit. Elektrochemie, **4**, 290 (1897).

formity of limiting values in non-aqueous solutions as is found in the case of aqueous solutions.

The degree of dissociation in aqueous solutions is calculated from either the boiling-point or cryoscopic determinations or from the electrical conductivity of the solution. These methods yield concordant results, but in non-aqueous solutions this is not the case.

In order to calculate the degree of dissociation from the electrical conductivity measurements it is necessary to know the value of μ_∞. It has been pointed out in the preceding that limiting values for μ are not always obtainable in non-aqueous solutions. In alcoholic solutions values for μ_∞ can generally be found. In the following table from Woelfer are given the values of the degree of dissociation, α, in methylic alcohol solutions as calculated from the boiling-point determinations of Woelfer, and from the conductivity measurements of Vollmer:

TABLE XXIII

Values of α

Salt	Percent	From boiling-point	From conductivity
LiCl	0.45	0.63	0.57
KI	0.36	0.61	0.79
NaI	0.44	0.87	0.74
CH_3COOK	0.48	0.48	0.63
CH_3COONa	0.40	0.49	0.63

The degrees of dissociation in methyl alcoholic solutions as calculated from the boiling-point determinations, show closer agreement with those obtained from the conductivity determinations than in the case of the other alcoholic solutions.

Salvadori[1] found $HgCl_2$ to be more highly dissociated in the methyl alcohol according to the boiling-point determinations than in aqueous solutions. Beckmann[2] found the reverse to be true in ethyl alcoholic solutions. Jones and King[3] calculated

[1] Gazz. Chim. Ital. **26**, I, 237 (1896). (Ref.) Jour. Chem. Soc. **70**, ii, 712 (1896).

[2] Zeit. phys. Chem. **6**, 437 (1890). [3] Am. Chem. Jour. **19**, 753 (1897).

the dissociation of KI in ethyl alcohol, from their boiling-point determinations, to be 25.4 percent in a 2 percent solution, and 27.2 percent in a 3 percent solution, i. e. the dissociation increases with the concentration. Cohen,[1] from the conductivity determinations at 18°, found the degree of dissociation of KI to increase with the dilution, being about 80 percent dissociated at a dilution of about 1000 liters. This disagreement of the dissociation values obtained by these two methods will be made more apparent perhaps by Table XXIV, which is copied from Woelfer's paper. The results by the boiling-point method were obtained by himself, those by the conductivity method by Vollmer.

TABLE XXIV

Values of *a*

Salt	Percent in ethyl alcohol	From boiling-point	From conductivity
LiCl	0.9	0.35	0.32
CH_3COOK	1.07	0.18	0.27
KI	0.78	0.29	0.49
$AgNO_3$	0.53	0.65	0.38
NaI	2.14	0.27	0.45
NaI	0.68	0.51	0.56
CH_3COONa	0.97	0.01	0.24

It is to be remembered that these two sets of values are calculated from results obtained at different temperatures; in the case of the conductivity measurements at 18°, when the viscosity factor is about 0.01211, and in the other case at 78° when that factor had decreased (at 70° to 0.00521). Yet it will be seen that there is no regularity of the results and that the degree of dissociation according to the boiling-point determinations is not invariably higher than that obtained by the conductivity method. It is no doubt but natural to ask, which of these methods gives the correct measure of the amount of dissociation of the dissolved substances.

There have been too few molecules weight determinations of salts in the ketones made by the boiling-point method. This

[1] loc. cit.

method, according to Dutoit and Friderich[1], yields normal molecular weights for a number of salts when dissolved in acetone. These substances, with the exception of LiCl and CdI_2, yield solutions that conduct fairly well. This would tend to indicate that they are quite highly dissociated while the boiling-point determinations indicate that they are not dissociated.

Attention has already been called to the fact of the conductivity of ferric chloride in nitrobenzene while the cryoscopic determinations indicate higher molecular weights than the theoretical.

In benzonitrile Werner[2] found normal molecular weights for $AgNO_3$ while from Table XVII it will be seen that this solvent yields solutions of $AgNO_3$ that conduct well. It still remains to be seen what the molecular condition of substances in other nitriles is according to the boiling-point determinations.

Werner's boiling-point determinations show normal molecular weights for the salts of the heavy metals in pyridine. The average of his determinations for $AgNO_3$ is 165.4, theory 169.55; for $Hg(CN)_2$, 216.68, theory 251.76; for HgI_2, 308.0, theory 452.88; and for $Pb(NO_3)_2$, 352.07, theory requires 330.35. In most cases he obtained values a little under the theoretical. The greatest discrepancy occurs in the case of $HgCl_2$, and it will be observed that the solution of this salt yields small values for μ. From Table XVIII it will be observed that this solvent yields conducting solutions and since μ_∞ is not known the degree of dissociation cannot be calculated.

From the preceding consideration it is apparent that there is not that agreement between the degrees of dissociation as calculated from the boiling-point or cryoscopic determinations and from the conductivity measurements in non-aqueous solutions as has been found to hold in aqueous solutions.

In aqueous solutions the molecular conductivity always increases with the dilution. From the analogy of the electrolytic dissociation of substances in aqueous solutions to the dissociation

[1] Bull. Soc. Chim. Paris (3) **19**, 321 (1898).
[2] Zeit. anorg. Chem. **15**, 1 (1897).

of gases, Ostwald formulated a law of dilution for binary electrolytes which is as follows: $K = \frac{a^2}{(1-a)V}$; where $a = \frac{\mu_v}{\mu_\infty}$ and V is the volume in which one gram-molecule of the dissolved substance is contained. In aqueous solutions of weak electrolytes this law generally holds fairly well; and attempts have been made to apply it to non-aqueous solutions. Most investigators, Vollmer, Woelfer, Cattaneo, and others have found that Ostwald's dilution law does not hold for methyl and ethyl alcoholic solutions. Cohen has considered this subject at considerable length and comes to the same conclusion.

Rudolphi's formula, which differs from Ostwald's in having $\sqrt{V}$ for V, has been shown to hold no better than Ostwald's. The values of the constant as calculated by these two formulae from the conductivity determinations of potassium acetate are given in the following table which is taken from Cohen's article. K_R indicates that those values were obtained by using Rudolphi's formula while K_o indicates that Ostwald's was employed.

TABLE XXV.

V	μ	$100\ K_R$	$100\ K_o$
11.4	8.28	0.82	0.242
113.0	17.18	0.59	0.055
1120.0	27.00	0.49	0.014
3520.0	29.20	0.36	0.006

From the preceding it therefore appears that neither the dilution law of Ostwald nor that of Rudolphi holds for alcoholic solutions. It has been shown in the case of propyl alcoholic solutions that we are not justified in extrapolating values for μ_∞, hence the validity of the law of Ostwald and that of Rudolphi cannot be tested in regard to this solvent nor are the data sufficient to warrant conclusions being drawn concerning the applicability of these laws to other alcoholic solutions.

From Fig. IV it will be observed that the molecular conductivity increases with the dilution except in the case of CdI_2 in acetone. The value of μ remains virtually constant and Dutoit and Friderich found the same to be true for solutions of

this salt in acetophenone. In the case of solutions of CdI_2 in methyl-propyl ketone and methyl-ethyl ketone the conductivity decreases with the dilution and the same was found by us to be the case for stannous chloride in acetone. Euler[1] found the molecular conductivity of both NaI and NaBr in benzonitrile to decrease with the dilution. The conductivity of ferric chloride solutions in benzaldehyde decreases with the dilution and the same is true of solutions in pyridine. Silver nitrate in piperidine yields solutions the conductivity of which decreases with the dilution.

In face of these experimental results and in view of the fact that in non-aqueous solutions there are but few cases where values for μ_∞ can be obtained, it appears that neither the dilution law of Ostwald nor that of Rudolphi can hold in non-aqueous solutions.

In general the conductivity of non-aqueous solutions increases with the increase of the temperature. There are no exceptions to this in aqueous solutions, but in non-aqueous solutions there are a few. The molecular conductivity of solutions of CdI_2 in acetone remains the same at 50° as at 25° ; but it must also be remembered that the conductivity of this salt does not change with the dilution. Solutions of CdI_2 in acetonitrile yield virtually the same values of μ at 0.2° as at 37.2°. The values of μ for $SbCl_3$ in paraldehyde are practically the same at 25.2° as at 32°. In ethyl benzoate the conductivity of solutions of $FeCl_3$ decreases from 1.55 at 25° to 0.48 at 100°, and the conductivity of solutions of $FeCl_3$ in amyl nitrite is practically constant at all temperatures tested.

There are not sufficient data to determine accurately the temperature coefficient of most of the non-aqueous solutions and particularly of the alcoholic solutions with which the most work has been done. But it can be stated that, in general, the conductivity does not increase proportionately with the temperature. It has been pointed out by Zelinsky and Krapiwin and later it has been confirmed by Cohen, as well as by Walker and Ham-

[1] Zeit. phys. Chem. **28**, 619 (1899).

bly,[1] that the temperature coefficient seems to be but slightly influenced by the addition of a non-electrolyte or even of a small quantity of water.

Although this investigation has been confined to the study of the conductivity of anhydrous salts and solvents it may be of interest to call attention to the work of some investigators on mixtures of water and alcohol. The following table of comparative conductivities is taken from the work of Zelinsky and Krapiwin. In the column headed A is given the conductivity in aqueous solutions, under B in methyl alcoholic solutions and under C is given the conductivity in a 50 percent solution of methyl alcohol and water.

TABLE XXVI

	KBr			NH_4Br		
v	A	B	C	A	B	C
16	123.1	....	59.82	127.2	65.43	61.16
32	127.5	69.02	62.46	131.8	72.73	63.81
64	130.5	76.70	65.36	135.3	79.56	66.04
128	132.9	83.60	67.11	138.6	85.80	67.45
256	136.4	88.96	69.26	141.2	90.88	68.32
512	140.2	93.26	70.53	143.5	94.99	69.10
1024	143.4	97.25	....	145.6	98.24	70.11
	KI			NH_4I		
v	A	B	C	A	B	C
16	124.5	69.20	62.13	125.4	72.24	62.63
32	128.2	76.35	64.37	129.6	78.74	65.04
64	130.5	82.52	66.01	133.4	85.0	67.48
128	133.0	88.69	67.45	135.9	91.14	69.28
256	135.8	93.85	68.28	138.7	96.20	70.34
512	137.9	98.19	69.65	141.3	100.6	71.12
1024	140.9	102.2	70.55	143.7	104.7	71.57

It will be noticed that the conductivity of the halogen salts of the alkalies in methyl alcohol (B) is considerably less than in aqueous solutions (A). When water is added to the extent of 50 percent even (C), the molecular conductivity is somewhat less than it is in methyl alcohol. Cohen and others have pointed out the same fact; that is, at 18° the conductivity of a mixture of water and alcohol, containing more than 60 percent of alcohol,

[1] Jour. Chem. Soc. **71**, i, 66 (1897).

is less in dilute solution than in absolute alcohol. This fact seems to be rather difficult to reconcile with the electrolytic dissociation theory, for here we have two solvents that possess dissociative power in a high degree, and yet a salt dissolved in a mixture of equal parts of these yields a solution the conductivity of which is less than that of the solutions formed when dissolved in either.

Carrara[1] has shown that the electrolytic dissociation of water in methyl alcohol is greater than in aqueous solutions, while the reverse is the case in ethyl alcohol. It is also of interest to note that KOH and NaOH in methyl alcohol show the same conductivity as CH_3OK and CH_3ONa.

As has been previously noted,[2] Nernst calls attention to the fact that solvents which have a high specific inductive capacity, yield solutions that conduct; and he argues that the greater the dielectric constant of a solvent, the greater is the power of dissociation. In general, those solvents that have a high dielectric constant do yield solutions that conduct, but the molecular conductivity is not commensurate with the dielectric constant. Lithium chloride in an aqueous solution (dielectric constant of H_2O is 78), gives a value of 95 for μ_∞ at 18°; while in propyl alcohol (dielectric constant is 20.45) in a volume of about 3000 liters, the value of μ at 15° is given as 128.9. In fact, most of the values of μ in dilute solutions of propyl alcohol are, according to Schlamp, greater than the values of μ_∞ in water. In methyl alcohol (dielectric constant is 32.65) the value for μ_∞ for $N(C_2H_5)_4I$ is 113.8, while in water it is 107.6; for $N(CH_3)_4I$ the values of μ_∞ in both solvents are virtually the same (115.3). In other alcoholic solutions the values of μ do not even approximate to those in aqueous solutions, however.

Esters, the dielectric constants of which are very low, yield solutions that conduct,—for example—ethyl oxalate, ethyl benzoate, and ethyl acetate. Attention has previously been called[3]

[1] Gazz. Chim. Ital. **27**, I, 422 (1897). (Ref.) Jour. Chem. Soc. **72**, ii, 473 (1897).

[2] Jour. Phys. Chem. **3**, 12 (1899).

[3] Ibid. **3**, 21 (1899).

to the fact that ethyl acetoacetate yields solutions of ferric chloride that conduct better than those in ethyl cyanacetate, the dielectric constant of the latter being 26.7, while that of the former is only 15.7. The values of μ in acetone approximate to and in some cases exceed the values in methyl alcoholic solutions. Benzonitrile was the only nitrile the dielectric constant of which could be found in the literature, but it is probable that the value of the other constants is relatively high. The value of μ for acetonitrile solutions approximate closely to those obtained for aqueous solutions, while for $CNS.NH_4$ and NaI, μ is of about the same magnitude as for $AgNO_3$ in benzonitrile. The dielectric constants of pyridine, piperidine and of quinoline could not be found in the literature.

From these considerations it therefore appears that while those solvents which have a high specific inductive capacity are the ones which, in general, yield solutions that conduct the best, the magnitude of μ is not proportional to the value of the dielectric constants.

Dutoit and Friderich,[1] from the results of other investigators and from their own researches on the ketones and nitriles, conclude that "*la conductibilité des electrolytes dissous dans un dissolvant non polymérisé est null.*" The degree of accuracy of this statement will become manifest when the following table is examined. In Table XXVII are arranged the names of a number of solvents in the order of increasing coefficients of association. The names appear in the first column, the coefficients of association in the second. These values were mostly determined by Ramsay and Shields (See Table I). The third column contains the viscosity factors, η, as far as they could be obtained from the tables of Dutoit and Friderich and of Landolt and Börnstein. The last three columns contain the formulæ of the salts, the volume in liters in which one gram-molecule was dissolved, and the molecular conductivity at that particular concentration. That salt was usually chosen which gave the largest value for μ.

[1] Bull Soc. Chim. Paris, (3) **19**, 321, (1898).

TABLE XXVII

Solvent	Coefficient of association	Dielectric constant (Air = 1)	η	Salt	v	μ
Quinoline	0.81	....	....	$AgNO_3$	129.8	3.62
Paraldehyde	0.85	....	....	$FeCl_3$	575.5	17.00
Pyridine	0.93	....	....	NH_4I	2528.6	41.00
Nitrobenzene	0.93	32.19	....	$FeCl_3$	1451.9	20.80
Ethyl acetoacetate	0.96	15.70	....	$FeCl_3$	503.5	23.40
Benzonitrile	0.97	26.00	....	$AgNO_3$	803.0	21.64
Benzaldehyde	0.97	14.48	....	$FeCl_3$	25.6	14.30
Phosphorus trichloride	1.02	....	....	....	....	....
Aniline	1.05	7.50	....	....	....	....
Acetophenone	1.05	16.40	....	$FeCl_3$	293.0	13.00
Carbon disulphide	1.07	2.61	0.00357	....	....	....
Piperidine	1.08	....	....	$AgNO_3$	4.24	0.37
Methyl-propyl ketone	1.11	16.75	0.0044	$AgNO_3$	1074.0	59.50
Methyl-ethyl ketone	1.15	18.44	0.0041	$CNS.NH_4$	94.8	19.70
Butyronitrile	1.22	....	0.0056	$AgNO_3$	150.4	32.10
Acetone	1.26	21.85	0.0031	KI	2315.2	153.20
Propionitrile	1.40	....	0.0040	$AgNO_3$	256.0	38.86
Acetonitrile	1.60	....	0.0033	$AgNO_3$	1141.4	159.30
Allyl alcohol	1.88	21.60	0.0130	$FeCl_3$	115.6	32.20
Propyl alcohol	2.25	20.45	0.0200	NaI	4495.5	174.70
Ethyl alcohol	2.74	25.70	0.0109	KI	∞	46.00
Methyl alcohol	3.43	32.65	0.0055	KI	∞	89.60
Water	3.60	78.00	0.0089	KI	∞	142.60

It will be observed that those solvents down to and including benzaldehyde, are not polymerized liquids according to the values of their coefficients of association, and they all produce solutions that conduct electricity. Among these are benzaldehyde and paraldehyde, both of which yield solutions that conduct well. Benzonitrile, the coefficient of association of which, even according to Traube, shows virtually no polymerization, yields solutions that conduct very well; and according to Werner gives normal molecular weights by the boiling-point method. Further, ethyl acetoacetate yields solutions that conduct very well; yet its molecules are not polymerized. It will also be noted that all of these solvents have relatively high dielectric constants. Solutions in nitrobenzene conduct; but according to Ramsey and Shields its molecules are not polymerized. Traube, however, gives a value of 1.47 for the coefficient of association of this substance. Of the organic bases quinoline yields solutions that conduct and shows the lowest degree of association of any of the solvents. Pyridine dissolves a large number of salts, and yields solutions that conduct; yet its molecules are not polymerized. It will be seen that the group of solvents whose coefficients of association are between 1 and 1.08 inclusive, thus indicating a very slight degree of polymerization, yield solutions that conduct slightly, and Ramsey and Shields regard most of these as non-polymerized liquids. Aniline yields solutions that conduct, particularly solutions of silver nitrate; acetophenone solutions do not conduct very well; and those in piperidine conduct poorly; while phosphorus trichloride and carbon disulphide, whose molecules are slightly polymerized, do not yield solutions that conduct electricity.

The molecular conductivity of solutions of different solvents is not commensurate with the degree of polymerization of their molecules. The examples given to illustrate that the molecular conductivity is not proportional to the dielectric constants of the solvents are applicable here as well. The value of μ depends, however, to a great extent upon the salts chosen; for example, the molecular conductivity of CdI_2 is virtually constant (11.7) in

acetone and in propionitrile it is 19.2 at dilution 512 liters; while the molecular conductivity of silver nitrate is 35 in ethyl alcohol at dilution 41,000 liters and 159 in acetonitrile at 1,141 liters. The coefficient of association of ethyl alcohol is 2.74 and that of acetonitrile is 1.60.

The coefficients of association as determined by Ramsey and Shields have been employed in preference to those by Traube[1] because the method of the former has a better theoretical basis, and their results are more in accord with those of other investigators. Traube gives for the value of the coefficient of association for benzene 1.18, for toluene 1.08, for ethylene chloride 1.46; and not any of these solvents yield solutions that conduct electricity. Then he gives values for the esters that are very much in excess of the determinations of other investigators, whereas the values for the alcohols are very much less. For example, for methyl alcohol he gives as the coefficient of association 1.79, for ethyl alcohol 1.67, for propyl alcohol 1.55, and for water 3.06. (Compare with the values given in Table I.)

Many solvents, whose molecules are polymerized, yield solutions that conduct electricity, and there are some whose molecules are supposed to be polymerized that do not yield solutions that conduct; and if Traube's results be taken, a large addition to those cited above could be given. It has also been pointed out that there are a considerable number of solvents, whose molecules are apparently not polymerized, yet whose solutions conduct electricity well,—for example, benzonitrile, ethyl acetoacetate, etc.

From the considerations presented in the preceding it appears that the theory as promulgated by Dutoit and Friderich, that only polymerized solvents yield solutions that conduct, is untenable.

Sometime before Dutoit and Friderich published their conclusions, Crompton[2] assigned a wider rôle to the associative property of liquids. He presents the view, that by means of this

[1] Ber. chem. Ges. Berlin, **30**, 273–4 (1897).

[2] Jour. Chem. Soc. **71**, ii, 925 (1897).

theory of association the anomalous results obtained in the case of certain dissolved substances, electrolytes, by the boiling-point, freezing-point and osmotic pressure determinations, can be easily explained; and aims to show that the electrolytic dissociation theory is not only unnecessary but in many respects inadequate. As has been previously pointed out no proportionality exists between the values of the dielectric constants of the solvents and the molecular conductivity of their solutions. Crompton calls attention to the connection between the specific inductive capacity and the degree of association of the solvents. This parallelism has also been pointed out by Abegg[1] who further observes that nitrobenzene, ethyl nitrite and benzonitrile all have high dielectric constants; yet their association factor is unity. This, he thinks, fulfills the primary conditions of a self-dissociating substance. Crompton further states: "It is almost impossible to doubt that association plays an all-important part in determining the value of the specific inductive capacity of a liquid, and that if there is any connection between the specific inductive capacity and the power of forming electrolytes, it may be looked for rather in the fact that electrolytes are solutions of approximately monomolecular salts in an associated solvent, than in there being any peculiar 'dissociative power' attached to the solvent." From the experimental results herein presented it appears that it is a *fact*, that *all* solvents that yield solutions which conduct are *not associated* liquids.

Crompton further aims to explain the conductivity of fused salts upon the dissociation of the associated molecules of the fused salts, wherein a small proportion of the salt is in the monomolecular condition. Abegg, however, shows that in many cases the melted salt has a higher dielectric constant than its "ice,"—for example, the dielectric constant of water is 78 while that of ice is 2.85 according to Thwing; and that in these fused salts the self-ionization or self-dissociation is very slight. He states that in about 100 liters of fused AgCl there is about one gram-molecule of AgCl completely dissociated. Kohlrausch[2]

[1] Zeit. Electrochemie, **5**, 48 (1899).

[2] Wied. Ann. **53**, 209 (1894).

has shown that in about eleven million liters of water there is one gram of hydrogen ions; while in methyl alcohol Carrara[1] found one gram-molecule of methyl alcohol dissociated in about five and a half million liters. If water and methyl alcohol manifest such great dissociative power upon salts dissolved in them, why is it that they do not dissociate their own molecules to a greater extent?

It is quite noticeable, that a large number of the investigators of the properties of non-aqueous solutions, express the thought that there is manifested considerable influence between the dissolved substance and the solvent. This factor of the influence of the solvent upon the dissolved substance, is one that is no doubt of very great importance; and in the development of the electrolytic dissociation theory(which is based upon the behavior of aqueous solutions) the action of the solvent upon the dissolved substance has been entirely neglected. The opponents of the dissociation theory present this fact in rather forcible manner.[2]

Fitzpatrick[3] concludes from his investigation on the conductivity of alcoholic solutions that the action of the solvent upon the dissolved substance is a chemical one. He conceives the dissolved salt as decomposing and forming molecular groups in the solvent. Owing to the large excess of the solvent there will be a continual decomposition and recombination of these molecular groups. He cautions one against regarding the solvent as a medium in which the salt particles are suspended or as a dissociating agent. Wildermann,[4] on the other hand, recognizes two kinds of dissociation—one, the electrolytic dissociation of the dissolved substance, and the other, the dissociation of the larger molecular aggregates into smaller ones. For example, in a solution of KCl in water the following aggregates are assumed to exist: K_2Cl_2, KCl, $K_2^{+}Cl$, $K\bar{Cl}_2$, $\dot{K}$ and $\bar{Cl}$. He

[1] Gazz. Chim. Ital. **27**, I, 422 (1897). (Ref.) Jour. Chem. Soc. **72**, ii, 473 (1897).

[2] Fitzgerald's "Helmholtz' Memorial Lecture" Jour. Chem. Soc. **69**, i, 885 (1896).

[3] loc. cit.

[4] Ber. chem. Ges. Berlin, **26**, 1773, 2881 (1893).

further maintains that solutions of all substances, whatever the solvent or the concentration, undergo electrolytic dissociation.

Cattaneo[1] was impressed with the fact that the molecular conductivity is greatly influenced by the nature of the solvent employed. He was not able, however, to point out any direct relation existing between the various properties of the solvents which yield solutions that conduct electricity. Konovaloff[2] from his work on the amines, concludes that only those solvents that react chemically with the dissolved substances yield solutions that conduct. It is true that there are many solvents of this nature which do react with the dissolved substance, and yet which do not yield solutions that conduct electricity. Picric acid reacts with benzene but the resulting solution does not conduct. Hence chemical combination of the dissolved substance with the solvent may take place and yet the solutions need not necessarily conduct. Werner[3] has isolated and analyzed a large number of products of pyridine and piperidine among other organic solvents, with salts of the heavy metals. From the boiling-point determinations, the molecular weights of these salts seem to be very slightly influenced by their union with the solvent. This is analogous to the fact, that salts which crystallize from an aqueous solution with water of crystallization, yield the same molecular weight whether dissolved in the anhydrous form or with their water of crystallization. Carrara thinks that the union of solvent and dissolved substance accounts for the slight conductivity in certain cases. The low values of μ in the case of acetone solutions of hydrochloric acid and lithium chloride he attributes to this fact.

It has been pointed out by Ciamician[4] that the dissociative power of a solvent depends principally upon its chemical structure. That is, compounds of the same chemical type, for example, of the HOH type, yield solutions that conduct electricity

[1] Rend. Accad. Linc, (5) **4**, II, 63. 73 (1895). (Ref.) Jour. Chem. Soc. **72**, ii, 537 (1897).

[2] Wied. Ann. **49**, 733 (1893).

[3] loc. cit.

[4] Zeit. phys. Chem. **6**, 403 (1890).

well. This is true in the case of alcoholic solutions, which are not the only class of compounds, however, that possess dissociative power, as has already been pointed out. In general, however, if one member of a particular type of compounds (e. g. nitriles) yield solutions that conduct, it has been found that other members also possess this property; and if a member of some other type (e. g. hydrocarbons) is found not to yield solutions that conduct, other members do not possess dissociative power.

The data collected are as yet insufficient to show what the relation between solvent and dissolved substance must be in order to yield solutions that conduct electricity. Enough facts have been presented, however, to make it apparent that any theory that aims to explain the electrical conductivity of solutions in general, must take into consideration the influence of the solvent upon the dissolved substance. This subject is replete with interest, for closely connected with it is the true cause of the solubility of substances.

From the foregoing the following general statements may be made:

1. In methyl and ethyl alcoholic solutions limiting values for μ can usually be obtained. The salts of the heavy metals are apparently exceptions. In other solvents a limiting value is very seldom obtained.

2. The degrees of dissociation of the dissolved substances in non-aqueous solutions, as calculated from the boiling-point or cryoscopic determinations and from the conductivity measurements, show very great disagreement. No such agreement is manifest as is observed in the case of aqueous solutions.

3. Neither the dilution law of Ostwald nor that of Rudolphi holds in the case of alcoholic solutions. In other solvents (since the conductivity remains virtually constant in some cases with the increased dilution, while in others it decreases) it is very apparent that the above-named laws do not hold. Then, too, since the value of μ_∞ cannot be obtained in the case of so many solvents, the validity of the dilution laws could not be tested.

4. The molecular conductivity, in general, increases with the dilution; but in several cases the conductivity decreases with the successive dilutions.

5. The molecular conductivity usually increases with the temperature, but not proportionally. In some cases it remains virtually constant with increase of temperature, while in others it decreases. The changes in the viscosity accompanying a varying temperature have not been determined.

6. Solvents that have a high dielectric constant yield solutions that conduct the best. Some solvents, the dielectric constants of which are very low, give poorly conducting solutions. The molecular conductivity is not, however, proportional to the dielectric constant of the solvent.

7. Some associated solvents yield solutions that conduct electricity, whereas others do not. Some solvents whose molecules are not polymerized yield conducting solutions. The value of μ, in those solutions that conduct, is not commensurate with the degree of association of the solvent.

8. The conductivity of electrolytes depends very much upon the nature of the solvent employed. No rigid classification can be made, but, in general, solutions in the hydrocarbons and their halogen substitution-products do not conduct. Alcoholic solutions conduct well, and the conductivity, in general, decreases with the increase of the carbon content. Solutions in esters conduct, but those of high carbon content usually yield solutions that conduct very poorly. The ketones and the aldehydes yield solutions that conduct well. Of the nitrogen compounds, liquid ammonia and ammonia substitution-products, or amines, conduct. The nitriles of both the aliphatic and aromatic series yield conducting solutions; and of the organic bases pyridine and quinoline come under this same category.

9. The dissociation theory as promulgated for the explanation of the electrical conductivity of aqueous solutions, apparently cannot be applied in its present form to explain the conductivity in non-aqueous solutions. It further appears that the auxiliary theories which are based upon the specific inductive capacity,

the polymerization of the molecules, and the self-ionization of the solvent, are not sufficient to explain satisfactorily the facts that have been accumulated. Notwithstanding the work that has been done, the data at hand are as yet insufficient for the formulation of a theory by means of which a satisfactory explanation can be given of the phenomenon of electrical conductivity of solutions in general.

This investigation was carried on under the supervision of Professor Kahlenberg, to whom I am under many obligations for his valuable suggestions, and I take this means of acknowledging the same.

Laboratory of Physical Chemistry, University of Wisconsin,
Madison, July 15, 1899.

CORRECTION

BY OSCAR LOEW

I find in an interesting article by J. F. Clark on "Electrolytic Dissociation and Toxic Effect" contained in the May number of the Journal of Physical Chemistry an erroneous statement which I desire to correct. On page 300 it reads: "Loew and Bokorny found that algae could use a one percent solution of formaldehyde for the production of starch." On the contrary we have been the first to demonstrate, with algae, the high toxic effect of formaldehyde on the simpler kinds of organisms. Even solutions of 1 : 10000 will kill algae. We have also shown that the combination of formaldehyde with primary sodium sulfite forms a harmless salt which can be substituted as a nutrient for algae and lower fungi. Perhaps it was this observation to which Clark referred.

Washington, D. C., July 15, 1899.

NEW BOOKS

Vorlesungen über theoretische und physikalische Chemie. *By J. H. van 't Hoff. Part II, Chemical Statics; 15 × 23 cm; pp. x and 148. Braunschweig: F. Vieweg und Sohn, 1899.* — This second part gives the substance of a course of lectures delivered in Berlin during the winter of 1897-98 and the summer of 1898. The first volume (**2**, 256) dealt with chemical dynamics and the present one treats of chemical statics. The first section of this little book is given up to molecular weights, how to determine them and the consequences to be drawn from these determinations. We have, therefore, Avogadro's law and methods of determining molecular weights of gases; Henry's law, Avogadro's law applied to solutions, and methods of determining molecular weights in solution. In the chapter on results we find, among other things, a discussion of the electrolytic dissociation theory and of the phenomena connected with solid solutions.

The second section of the work deals with molecular structure, including isomerism and tautomerism. Here we find a brief sketch of the methods of determining structure formulas with special reference to stereochemistry and to the decomposition of optically inactive into optically active substances. This is followed by a chapter on tautomerism which is not up to date. The work published since 1897 is almost completely ignored with the result that this chapter does not represent our knowledge of the subject.

The third section treats the equilibrium relations between different solid modifications when only one form exists in the melt or in solution, and the book closes with a chapter on crystallography.

Every reader will hail with delight the interweaving of organic chemistry and physical chemistry which we find in this volume. It must be clear, by this time, to many people that, sooner or later, organic chemistry must be revised by the physical chemist. The present system of structure formulas satisfies the needs of the qualitative chemist very fairly. While many chemists consider these formulas as representing the actual structure of the molecule, there is an ever-growing minority which takes them for what they are, a remarkably clear and concise method of epitomizing what we know. The structure formulas enable us then to tell, in a general way, what reactions will take place in any given case and what reaction products will be formed; but this information is purely qualitative. As organic chemistry changes gradually from a qualitative empiricism to a quantitative science, we shall feel the need of expressing these quantitative relations in a concise manner and we shall replace our qualitative shorthand by a quantitative shorthand. Of course, nothing of

this appears in these lectures. The time is not ripe for it, and the frankly atomistic point of view taken by the author would probably preclude it in any case; but the important point is for the physical chemist to feel that he must struggle with constitutional formulas, and in this van 't Hoff has set him an excellent example.

Wilder D. Bancroft

Lehrbuch der allgemeinen Chemie. *By W. Ostwald. Vol. II., Part 2. Instalment 4. 16 × 24 cm; pp. 605-828. Leipzig: W. Engelmann, 1899. Price: 5.40 marks.* — The number opens with a long and interesting discussion of the pressures and concentrations in the vapor phase for mixtures of two volatile liquids. It is admitted that, in general, Henry's law does not coincide with the van 't Hoff-Raoult formula. It would have been more interesting if the author had taken the van 't Hoff version of the formula with the logarithm of the pressure instead of the Raoult form. While the two are practically identical for very dilute solutions, this is no longer the case when the solutions become moderately concentrated. The treatment of fractional distillation is by far the most complete that has yet been given; but, as in all other textbooks, the theory of distillation with a still-head at constant temperature has been entirely overlooked. This is unfortunate, because this method is by far the most satisfactory when it comes to the actual separation of two liquids.

The development of the quantitative theory of binary mixtures, pp. 636–647, may be taken as a characteristic instance of Ostwald's genius as a teacher. It is not new, and it may not all be right; but it is put in a clear, intelligible fashion so that anyone can make out for himself just how matters stand.

The experiments of Kuenen on the phenomena near the critical temperature are considered at length, as are also Rothmund's measurements on the solubility curves for two partially miscible liquids. A couple of pages on the possibility of supersaturation phenomena with two liquids precedes the treatment of two liquid phases without vapor. In connection with this Ostwald mentions that no case is known where there are more liquid phases than there are components. This would imply that he considers Lehmann's flowing crystals as a solid phase and not as a crystalline liquid.

Some ninety pages are devoted to the question of solubility and of supersaturation phenomena. Here we have a most interesting presentation of the subject including a mass of forgotten observations. No one will deny that it is excellent reading; but one feels that it would have been better to have published a small monograph on the subject, if necessary, and then to have condensed that into a moderate number of pages in the textbook. As matters now stand there is no real proportion between the importance of a subject and the number of pages assigned to it.

The remainder of the number is devoted to a consideration of solubility curves in general, including melting-points of compounds, together with an analysis of the relations between solubility, pressure and heat effects.

Wilder D. Bancroft

Allgemeine und physikalische Chemie. *By Max Rudolphi. Sammlung Göschen, No. 71. 10 × 15 cm. 193 pp. Leipzig: G. J. Göschen. 1898. Price: cloth, 80 pf.* — The *Sammlung Göschen* is an admirable series of inexpensive

little editions of literary classics, and of treatises on various branches of science. The books are fairly well printed, are neatly bound in flexible cloth covers, and cost but eighty pfennigs—twenty cents—each. One of the more recent numbers is a volume on physical chemistry, by Max Rudolphi. It is about what would be obtained by condensing Nernst's well-known treatise to a small compass. Although some features of its execution are open to criticism, yet the material presented is calculated to give the intelligent general reader a fair idea of what ordinarily passes for physical chemistry,—and this is the object of the book. It may fairly be conceded that the little volume is well worth its price.

J. E. Trevor

Outlines of physical chemistry. *By A. Reychler; translated by J. McCrae. 12 × 19 cm; pp. xvi and 276. London: Whittaker & Co.; New York: The Macmillan Co., 1899. Price: cloth $1.00.* — The original French edition has already been reviewed (**2**, 195). The English edition is, however, a translation of an unpublished revision of the French work, and therefore corresponds to a second edition. The book is essentially a compilation by an outsider, and betrays that fact on almost every page. It is, however, well worth the price charged for it. There are now quite a number of books on physical chemistry in English. No one of them is very good, or even moderately satisfactory, but it seems reasonable to suppose that if a student were to read all of them carefully, he might then be able to separate some of the wheat from the chaff. There must come a time when some one will write a really first-class well-balanced book on physical chemistry in some language; but there are no signs of it as yet. It may be a little unreasonable to expect such a thing, since there is no corresponding work in organic or inorganic chemistry, and these branches of the subject have flourished for a much longer period than has physical chemistry.

Wilder D. Bancroft

Inorganic Chemistry according to the Periodic Law. *By F. P. Venable and J. L. Howe. 14 × 20 cm; pp. iv and 266. Easton: The Chemical Publishing Co., 1898. Price: cloth $1.50.* — To read the introduction of this book is suggestive of a search for information in a small dictionary, which after leading the investigator through circuitous paths of definition either abandons him in a blind alley, or conducts him craftily back to his original starting-point. "Chemistry," we are told, "is the study of matter and the changes produced in that matter by the action of chemical force upon it" We look for a definition of chemical force and all we find is "a primitive, permanent and constant force depending wholly on the nature of the unchangeable atom" (p. 15) while for "matter" we find the all-embracing statement that it is "that which occupies space." We look up *molecule* and discover it to be "the smallest particle of matter which still retains the properties of the mass," and that "it is too small to be appreciable to our senses," while turning to *mass* in the hope of finding these properties discussed we are discouraged by finding that it is "any form of matter which is appreciable to our senses."

After 30 odd pages of such disheartening reading we cannot but feel encouraged to find that some such difficulty was anticipated by the author. "This introduction contains, in outline, some of the great principles of the science.

It is scarcely expected that they will be fully grasped and comprehended by the student just entering upon the study. He is rather to look upon much of it as a statement of what is to be proved by further study. A good deal of it will be repeated in suitable places later when facts have been acquired which will render explanation possible. . . ." Unfortunately, however, or perhaps fortunately, the great principles of the science are left to themselves in the remaining part of the volume and consequently as a purely descriptive textbook it is excellent.

After looking in vain for such fundamental matters as Elements and Compounds and the determination of atomic weights, and after finding the first mention of reciprocal and multiple proportions seven pages from the close of the book, we expect at least to find an adequate treatment of the periodic law itself which purports to be the guiding principle of the whole work, but even this hardly does more for the book than upset the continuity of description. A few pages in the introduction, a few lines at the beginning of each group of elements, and an arrangement of the compounds of all the elements under general headings of hydrids, chlorids, etc., are all the honor done to the guiding principle. *Frank B. Kenrick*

Aufgaben über Wärme; einschliesslich der mechanischen Wärmetheorie und der kinetischen Theorie der Gase. *By Eduard Maiss. 13 × 21 cm; pp. iv and 118. Wien: A. Pichler's Witwe & Sohn, 1898. Price: paper 2.40 marks.* — In the present little volume, the author, a professor in a Vienna *Oberrealschule*, has assembled a series of problems for the use of students of the theory of heat. These problems relate to thermometric scales, the thermal expansion of solids, liquids, and gases, specific heats, fusion, vaporization, combustion, heat conduction, the equivalence of heat and work, and the kinetic theory of gases. The collection is of a practical character, and is altogether admirable. It is well selected and arranged, and is certain to be very instructive to the student who conscientiously works it through. It might be used to great advantage in instruction in physical chemistry. Complete solutions of all the problems are added at the close of the book. *J. E. Trevor*

Die fundamentalen physikalischen Eigenschaften der Krystalle. *By W. Voigt. 14 × 21 cm; pp. viii and 243. Leipzig: Veit & Co., 1898.* — This book is based on lectures delivered in Göttingen during the spring vacation of 1897. The discussion is limited to the fundamental physical properties of the crystals, i. e. to those which come into account during a homogeneous change of a crystal or crystal section. In the treatment the author distinguishes scalars, vectors and tensors, this last being a new term introduced by himself. Variables such as the temperature which can be described by a single numerical value are called scalars; those which can be described by a number and a single direction in space, are called vectors; while those, such as a tension, which can be described by a number and by a direction running symmetrically both ways from a point, are called tensors. Tensors might have been called bivectors; but there are distinct objections to this name.

The book consists of eight chapters: the physical symmetry of homogeneous crystalline matter; the physical properties as reciprocal relations between two states of matter; relations between a scalar and a vector; relations be-

tween a scalar and a tensor triplet (three tensors each normal to the others); relations between two vectors, especially between two similar vectors; relations between a vector and a tensor triplet; relations between two tensor triplets; physical properties of a higher order and those for which the laws have not yet been worked out. In addition there are thirteen appendices dealing with special points in crystallography and mathematical physics.

Wilder D. Bancroft

Michael Faraday, his Life and Work. (*The Century Science Series*). *By Silvanus P. Thompson. 13 × 19 cm; pp. ix and 308. New York: The Macmillan Co., 1898. Price: cloth $1.25.* — Professor Thompson's Life of Faraday is one of the most delightful biographies it has ever been our good fortune to read. With a glowing enthusiam for his subject, the author tells us as simple, sweet, and withal impressive, a tale as one could wish to hear; a tale that does justice to the sweetness and dignity of its subject.

The book begins with an account of Faraday's early life; and then considers successively his life at the Royal Institution, his scientific researches, his later years, his general attitude toward science and education, and his naive views on religion. Much interest attaches to the reproduction of a number of hitherto unpublished extracts from Faraday's laboratory notebooks, with accompanying facsimile sketches. The frontispiece of the book is a beautiful etching of Faraday, bearing the initials of the author.

In his preface, Professor Thompson says:

"For forty years Faraday was a living and inspiring voice in the Royal Institution, beyond all question the greatest scientific expositor of his time. Throughout almost the whole of that time his original researches in physics, and chiefly in electricity, were extending the boundaries of knowledge and laying the foundations not only for the great developments of electrical engineering of the last twenty years but for those still greater developments in the theories of electricity, magnetism, and light which are every year being extended and made fruitful. Were there no other reason than these developments in practice and theory, they would amply justify the effort to review now, after so many years, the position of Faraday amongst the eminent men of the century now drawing to its close.

"Those who were intimately acquainted with him are a fast dwindling band. In the recollection of such as have survived him, his image lives and moves, surrounded with gracious memories, a vivid personality instinct with rare and unselfish kindliness. But the survivors are few, and their ranks grow thinner with each succeeding year. And so it comes about that the task of writing of his life and work has been entrusted to one who never ceases to regret that he never met Faraday."

J. E. Trevor

A Text-book of Physics. Sound. *By J. H. Poynting and J. J. Thomson. 16 × 23 cm; pp. x and 163. Philadelphia: J. B. Lippincott Company, 1899. Price: cloth $3 00.* — It may confidently be anticipated that the forthcoming Textbook of Physics, by Professors J. H. Poynting and J. J. Thomson, will be a marked advance over the college textbooks of physics that we now have. The

collaboration of two such men of science in an undertaking of this sort cannot but yield a gratifying result.

The entire work is to consist of five parts,—on the properties of matter, sound, heat, magnetism and electricity, and light, respectively. Of these the volume on sound is now out. It is a compact, clear, and simple disquisition, which should be intelligible to anybody. The authors say that it is intended for students who lay most stress on the study of the experimental part of physics, and who have not yet reached the stage at which the reading of advanced treatises on special subjects is desirable. The treatment employs only elementary mathematical methods, since many students are unable to handle the advanced methods. The authors' hope is certainly justifiable, that their book will supply a fitting introduction to the more advanced treatises, especially to Helmholtz's 'Sensations of Tone,' and Rayleigh's 'Theory of Sound,' "at once the most systematic, original, and complete work on the subject."

J. E. Trevor

The Newer Remedies, *including their synonyms, sources, methods of preparation, solubilities, incompatibles, medicinal properties, and doses as far as known, together with sections on organo-therapeutic agents and indifferent compounds of iron. A reference manual for Physicians, Pharmacists, and Students. By Virgil Coblentz. 150 pp. Third, revised, edition. Philadelphia: P. Blakiston's Son and Co., 1899. Price: cloth $1.00.* — The constantly increasing number and complexity of the newer remedies render it necessary for the physician and apothecary to have some convenient book to which they can refer to inform themselves concerning these products. This the book of Dr. Coblentz supplies in a very satisfactory manner; otherwise three editions of the work would not have been called for since April 1895, when the first edition appeared. The book can be heartily recommended to all who wish to know anything about the newer remedies.

W. R. Orndorff

Some Notes on Chemical Jurisprudence. *By Harwood Huntington. 17 × 24 cm; 24 pp. New York. Price: paper $0.25.* — This little pamphlet is said to contain all or nearly all of the litigated cases in patent law where chemistry is involved, and there is certainly a great deal of interesting information to be found in it.

Wilder D. Bancroft

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry

General

New experiments on the quantitative synthesis of water. *E. H. Keiser. Am. Chem. Jour.* **20,** *733 (1898).* — Owing to the difficulty of obtaining complete combustion with a mixture of hydrogen and water, oxygen is brought in contact with palladium charged with a known weight of hydrogen. One method of calculating the results gave 15.874 for the ratio, while another method gave 15.886. The means of the two is 15.880. *W. D. B.*

A determination of the atomic weight of zinc. *H. N. Morse and H. B. Arbuckle. Am. Chem. Jour.* **20,** *195 (1898).* — A repetition of the work of Morse and Burton, especial attention being paid to the amount of gas occluded by the zinc oxid. The final value is Zn 65.457. *W. D. B.*

The atomic weight of cadmium. *H. N. Morse and H. B. Arbuckle. Am. Chem. Jour.* **20,** *536 (1898).*—A repetition of the work of Morse and Jones, especial attention being paid to the amount of gas occluded by the cadmium oxid. The final result is Cd 112.377. *W. D. B.*

A determination of the atomic weight of praseodymium, and of neodymium. *H. C. Jones. Am. Chem. Jour.* **20,** *345 (1898).*—The final results are praseodymium 140.45 and neodymium 143.6. *W. D. B.*

The atomic mass of tungsten and the preparation of sodium pertungstate by means of the electric current. *G. E. Thomas. Jour. Am. Chem. Soc.* **21,** *373 (1899).* — Reduction of tungsten trioxid gave 183.64 as the combining weight of tungsten while oxidation of tungsten leads to a value above 184. Determining the water of crystallization in sodium tungstate gave 184.7 with single values varying from 182.3 to 187.5.

Sodium pertungstate can be made conveniently electrolytically. The directions are pleasingly indefinite, the author giving values for current and voltage when the sodium tungstate solution is *not* in circuit. *W. D. B.*

The cyclical law of the elements. *T. Bayley. Jour. Am. Chem. Soc.* **20,** *127 (1898).* — It is claimed that more stress should be laid on the cyclical na-

ture of the periodic law and less on the fact that the first two complete series (or cycles) contain each seven elements. *W. D. B.*

Atomic volume as a periodic function. *T. Bailey. Jour. Am. Chem. Soc.* **20,** *935* (*1898*). — A study of atomic volumes bringing out the usual relations. *W. D. B.*

Helium. *W. Ramsay. Ann. Chim. Phys.* (*7*) **13,** *433* (*1898*). — This paper gives an extended account of the discovery and properties of helium. *W. D. B.*

A new gas. *C. F. Brush. Jour. Am. Chem. Soc.* **20,** *899* (*1898*). — It was found that a gas was given off by pulverized glass when the glass was placed under diminished pressure. When the pressure is reduced to a few millionths of an atmosphere this gas has a conductivity for heat one hundred times as great as that of hydrogen. The author proposes calling this new substance etherion. [It has since been suggested by Crookes and others that etherion is water vapor.] *W. D. B.*

On the claims of davyum to recognition as a chemical element. *J. W. Mallet. Am. Chem. Jour.* **20,** *776* (*1898*). — The author has repeated the work of Kern and finds that the so-called davyum is probably only a mixture of iridium and rhodium with a little iron. The spirit prompting Prof. Mallet to undertake this piece of work is a most commendable one. Of course, no one believed in the existence of davyum; but, on the other hand, no one knew what Kern had mistaken for a new element. It is unsatisfactory to undertake work that is practically certain to lead to a negative result, to a result that no one questioned. There are, however, many statements about the elements, especially about the allotropic modifications, which are probably false but which will continue to be stumbling-blocks until some one will sacrifice his time, as Prof. Mallet has done his, in order to clear these matters up. *W. D. B.*

A convenient gas generator and device for dissolving solids. *T. W. Richards. Am. Chem. Jour.* **20,** *189* (*1898*). — Various modifications of gas generators are described, the essential feature in each being that the spent acid settles to the bottom and can be drawn off there. By placing a solid in a funnel closed by glass wool at the bottom and sinking the whole under water, the solution sinks to the bottom of the vessel, fresh water flows in over the top of the funnel and the salt is dissolved in a much shorter time than if the crystals were at the bottom of the beaker. The solution is filtered at the same time. *W. D. B.*

Apparatus for determining the density of powders. *G. J. W. Bremer. Recueil Trav. Pays-Bas,* **17,** *263, 405* (*1898*). — The apparatus is based on the principle of comparing the changes of pressure when a known quantity of air is added first to a flask containing air, and then to the same flask containing the substance to be measured. The author claims several advantages for his instrument over those of Paalzow and of Baumhauer. *W. D. B.*

A new apparatus for the determination of volume. *C. F. McKenna. Jour. Am. Chem. Soc.* **21,** *50* (*1899*). — The apparatus consists essentially of a flask with one fine graduated neck and one wide neck. By means of a rubber bulb,

the liquid in the wide neck is blown to a certain mark, and the height of the liquid in the other arm read off. The solid is then introduced through the wide neck, the surface of the liquid brought to the original mark, and the new position in the narrow neck noted. *W. D. B.*

A simple volumenometer. *C. E. Linebarger. Jour. Am. Chem. Soc.* **21,** *435* (*1899*). — This instrument is identical in principle with that of McKenna (preceding review) but can be made from ordinary laboratory stock as it only calls for a graduated pipette, a wide mouthed bottle, and a funnel. *W. D. B.*

One-Component Systems.

Experiments on crystalline liquids. *R. Schenck. Zeit. phys. Chem.* **25,** *337;* **27,** *167* (*1898*); **28,** *280* (*1899*). — Three substances are known which form crystalline liquids or fluid crystals. If melted *p*-azoxyanisol be cooled to 134.1° a new phase appears which is a second liquid phase save that it is not isotropic. At 114° there is another triple point with solid crystals as the new phase. The same two changes occur with *p*-azoxyphenetol at 165.2° and 134.5°; with cholesteryl benzoate at 178° and 145.5°. In all three cases the anisotropic phase is less dense than the isotropic and with *p*-azoxyanisol it is less viscous. Judging from the surface-tension phenomena the anisotropic and the isotropic liquids have the same molecular weight in the cases of *p*-azoxyphenetol and *p*-azoxyanisol while the two forms of cholesteryl benzoate have different molecular weights. The inversion point of *p*-azoxyanisol is lowered to about the same extent by the addition of ethyl oxalate, benzyl acetate, diphenyl, *o*-dinitrobenzene, thymol, carvacrol and carvol. From these data the author calculates a heat of inversion of 4.42 cal. This calculation is permissible only in case the substances just mentioned do not affect the true freezing-point, a question that appears to have been overlooked by the author. Addition of *p*-azoxyphenetol or cholesteryl benzoate raises the inversion temperature.

In the third paper the author measures the specific heats of the anisotropic and isotropic liquids. From these data and the heat of inversion previously obtained he calculates the critical temperature and pressure for these two phases. This he is able to do approximately because he also determined the change of the inversion temperature with the pressure, finding a pressure of 13.2 atm necessary to cause a rise of one degree. *W. D. B.*

Theory of complete and pasty fusion. *M. Brillouin. Ann. Chim. Phys.* (7) **13,** *264* (*1898*). — The author points out that the substances that soften and become viscous on heating have no true melting-point. He expresses his disbelief in any continuous passage from solid to liquid. *W. D. B.*

On the liquefaction of hydrogen and helium. *J. Dewar. Ann. Chim. Phys.* (7) **14,** *145* (*1898*). — Reviewed (**2,** 505) from Jour. Chem. Soc. **73,** 528 (1898).

An alternating volatility in the series of the normal acid chlorids. *L. Henry. Bull. Acad. roy. Belg.* **1899,** *63*. — The boiling-points of normal acid chlorid containing $2n$C lie 26°–30° above those containing $2(n-1)$C.

On variations of volatility in the series of the normal acid chlorids. *L. Henry. Bull. Acad. roy. Belg.* **1899,** *63.* — The boiling-points of normal acid chlorids containing $2n$ combining weights of carbon are 26°–30° above those containing $2n-1$ combining weights and 16°–20° below those containing $2n+1$ combining weights. *W. D. B.*

On an isomer of potassium ferrocyanid. *J. Locke and G. H. Edwards. Am. Chem. Jour.* **21,** *193, 413 (1899).* — By treating a hot solution of potassium ferricyanid with potassium chlorate and hydrochloric acid, and cooling before the effervescence begins, the authors obtained a salt $K_4Fe(CN)_6H_2O$ which they call potassium β-ferrocyanid, the compound hitherto known being now called the α-ferrocyanid. The crystalline forms of the modifications are different and a freshly-prepared solution of the β-salt gives no precipitate with bismuth nitrate. Stannic chlorid precipitates a slimy green substance from a solution of the β-salt. The new modification passes over readily into the α form. In the second paper it is shown that the formation of the β-ferrocyanid is due to the catalytic action of hydrochloric acid and that the presence of potassium chlorate is unnecessary. *W. D. B.*

Trinitrophenylmalonic ester. *C. L. Jackson and J. I. Phinney. Am. Chem. Jour.* **21,** *418 (1899).* — This substance occurs in two forms, one melting at 58° and the other at 64°, the latter being the more stable. From the fact that "each form has been converted into a salt, and set free from this unaltered upon acidification" the authors incline to the belief that this is "a case of chemical rather than physical isomerism." They did not make the crucial test of determining whether the more stable form melted and froze sharply at the same temperature. If this is not the case there must be two modifications in the melt. This is an excellent instance of the advantage that might be gained by applying the methods of physical chemistry to organic chemistry.
W. D. B.

Study of the latent heats of vaporization of some liquids. *W. Louguinine. Ann. Chim. Phys. (7)* **13,** *289 (1898).* — The author has determined the specific heats between 20° and the boiling-points, the variation of the boiling-points with pressure, and the heats of vaporization of a number of alcohols, ketones and esters. The values for MS/T (Trouton's formula) are nearly identical at about 26 for all the alcohols except the two amyl alcohols. The ketones give values varying but little from 20.84 while the three esters measured are pretty constant at 21.8. The great discrepancy in the case of the alcohols is attributed to polymerization in the liquid state. *W. D. B.*

The specific gravity of cesium. *A. E. Menke. Jour. Am. Chem. Soc.* **21,** *420 (1899).* — The cesium used was purified by several redistillations in hydrogen, and then examined spectroscopically. The metal was weighed in hydrogen and then under liquid paraffin. The mean of six results was 2.40003 referred to water, at least four grams of metal being taken in each experiment. This makes the atomic volume of cesium 55.3 instead of 70.6 as usually given.
W. D. B.

Experiments on gases. *A. Leduc. Ann. Chim. Phys.* (*7*) **15,** *5* (1898). — This paper sums in a connected whole the substance of a number of short articles which have appeared in the Comptes rendus and which have been reviewed from that source. *W. D. B.*

Some properties of liquid ammonia. *E. C. Franklin and C. A. Kraus. Am. Chem. Jour.* **21,** *8* (*1899*). — The close resemblance between water and ammonia is emphasized by a discussion of the physical properties of these two liquids. *W. D. B.*

Two-Component Systems

Equilibria between ammonium nitrate and ammonia. *B. Kuriloff. Zeit. phys. Chem.* **25,** *107* (*1898*). — The author has determined the solubility curve for ammonium nitrate and liquid ammonia from $-60°$ to $+168°$. One compound occurs, probably $NH_4NO_3{,}3NH_3$ with a melting-point of about $-40°$. Above this temperature the only solid phase is NH_4NO_3 (See **3,** 178). *W. D. B.*

Addition to paper on the freezing-points of pure palmitic and stearic acids and of their mixtures. *L. E. O. de Visser. Recueil. Trav. Pays-Bas,* **17,** *346* (*1898*). — In a previous paper (**2,** 506) it was shown that a solution containing 47.5 percent stearic acid solidified without change of temperature although not the eutectic mixture. In this note it is shown that the presence of alcohol does not displace this equilibrium. From this it is concluded that a solid solution separates from a mixture of the two acids and that the solid solution has the same composition as the liquid solution when the latter contains 47.5 percent of stearic acid. The conclusion is undoubtedly right but the reasoning is entirely wrong because the experiment with alcohol, though interesting, proves absolutely nothing in regard to this point. *W. D. B.*

The transition temperature of sodic sulphate, a new mixed point in thermometry. *T. W. Richards. Am. Jour. Sci.* (*4*) **6,** *201* (*1898*). — Reviewed (**3,** 177) from Zeit. phys. Chem. **26,** 690 (1898).

On the relation between heat of solution, solubility, and degree of dissociation. *H. Goldschmidt. Zeit. phys. Chem.* **25,** *91* (*1898*). — Van't Hoff has given the formula

$$\frac{\partial \log C}{\partial T} = \frac{q}{2iT^2}$$

where C is the solubility, q the heat of solution and i the isotonic coefficient. Van Laar writes the formula

$$\frac{\partial \log C}{\partial T} = \frac{q}{2T^2} \cdot \frac{2-a}{2}$$

where a is the degree of dissociation.

In order to compare these two formulas the solubilities and heats of solutions of silver acetate, silver propionate, silver isobutyrate and *o*-nitrobenzoic acid were determined. The amount of dissociation was obtained from conductivity measurements. Neither the van 't Hoff nor the Van Laar formula were

very satisfactory with the three silver salts. The van Laar formula gave much better results when applied to *o*-nitrobenzoic acid than did the van 't Hoff formula. *W. D. B.*

Studies on the nitrobenzoic acids. *A. F. Holleman. Recueil Trav. Pays-Bas*, **17**, *247, 329, 335 (1898).* — The author has determined the solubility of the three nitrobenzoic acids at three temperatures in water, chloroform, and alcohol. In water the ortho acid is the most soluble and the para acid the least soluble. In chloroform and in alcohol the meta acid is the most soluble and the para acid the least soluble. When mixtures of the ortho and para acids or of the meta and para acids were treated with water, it was found that the solubility of each acid had been decreased by the presence of the other. An increased solubility was observed when a mixture of ortho and meta acids was taken. Since it has been shown that the formation of a compound in solution will account for an increased solubility, the conclusion is therefore drawn that the ortho and meta acids form a compound in solution. From this is deduced the surprising conclusion that there must be a change in the nature of the solid phase. Experiments are then carried out which prove the accuracy of this view to the author's satisfaction without, however, throwing any light on the question of what the new phase may be. *W. D. B.*

Liquid ammonia as a solvent. *E. C. Franklin and C. A. Kraus. Am. Chem. Jour.* **20**, *820 (1898).* — The authors have made qualitative determinations of the solubility in liquid ammonia of some five hundred different substances. *W. D. B.*

Determination of the molecular rise in the boiling-point of liquid ammonia. *E. C. Franklin and C. A. Kraus. Am. Chem. Jour.* **20**, *836 (1898).* — A Dewar vacuum tube was used as the boiling-tube and the ammonia was heated by an electric current. The constant for water is 3.4; for ethyl alcohol 3.4; for propyl alcohol 3.4 in moderately dilute solutions, decreasing to 2.75 in more concentrated solutions. The value for phenol is 3.0; for pyrocatechin 3.2; for resorcin 3.5 and for hydroquinone a little higher. With cane sugar the constant increases with the concentration from 3.0 to 4.7 while with urea the value decreases from 3.4 to 2.3. Pyridin gives 3.2, dropping to 1.8 for very concentrated solutions. Orthonitrophenol gives about 3.4 while the value for benzene is 2.5 in moderately dilute solutions. Ammonium nitrate, sodium nitrate and potassium iodid give values of 2.0 or less for moderately dilute solutions increasing to over 5.0 for more concentrated solutions. If it be assumed that with potassium iodid we have $KI7NH_3$ in solution, the values become quite constant at about 3.4. Sodium gives values varying from 1.50 to 2.50 while with lithium the molecular rise is only about 1.35. *W. D. B.*

Molecular weights of liquids. III. *C. L. Speyers. Jour. Am. Chem. Soc.* **21**, *282 (1899).* — The results of Lehfeldt are discussed. The conclusions are interesting but are faulty in two respects. An inaccurate formula is used, $n_1/(n_1 + n_2) = (p - p')/p$, and the author does not differentiate the cases in which the apparent association varies with the concentration from those in which it does not. These two sources of error, and the complete ignoring of

Henry's law make these papers (See **2**, 347, 362) less valuable than they otherwise might be. *W. D. B.*

Dissociation of phosphorus pentabromide in solution in organic solvents. *J. H. Kastle and W. A. Beatty. Am. Chem. Jour.* **21**, *392* (*1899*). — Judging from the color phosphorus pentabromid is ninety to one hundred percent dissociated into phosphorus tribromid and bromin in dilute carbon bisulfid solution, and eighty to ninety percent dissociated in carbon tetrachlorid solution. *W. D. B.*

On some double halides of mercury. *J. N. Swan. Am. Chem. Jour.* **20**, *613* (*1898*). — An account of some crystalline compounds of mercuric chlorid with anilin, orthotoluidin, metatoluidin, and paratoluidin. The experimental work was finished early in 1893. *W. D. B.*

The double halides of tin with aniline and the toluidines. *R. L. Slagle. Am. Chem. Jour.* **20**, *633* (*1898*). — This paper differs from that of Swan (preceding review) in that stannous chlorid is substituted for mercuric chlorid. The work was finished early in 1894. *W. D. B.*

On double halides of zinc with aniline and the toluidines. *D. Base. Am. Chem. Jour.* **20**, *646* (*1898*). — Further work (cf. preceding two reviews) confirming Remsen's law. This paper dates from 1895. *W. D. B.*

Experiments on ozone. *M. Otto. Ann. Chim. Phys.* (*7*) **13**, *77* (*1898*). — By using a specially designed ozonizer, an alternating current with eighty periods per second, and a potential difference of 6500 volts, eight to ten times the usual yield of ozone was obtained. *W. D. B.*

On the heat evolved by the action of small quantities of water on a large excess of sulfuric acid. *M. Berthelot. Ann. Chim. Phys.* (*7*) **13**, *77* (*1898*). — Heats of dilution when one, two, three and four of water are added to twenty of sulfuric acid. *W. D. B.*

On the heat disengaged by the action of small quantities of water on an excess of nitric acid. *M. Berthelot. Ann. Chim. Phys.* (*7*) **14**, *207* (*1898*). — Heats of dilution when one, two and three of water are added to $31.44HNO_3$. *W. D. B.*

Poly-Component Systems.

Investigations on the formation of oceanic salt deposits, with special reference to those at Stassfurt. I, II, III. *J. H. van't Hoff and W. Meyerhoffer. Sitzungsber Akad. Wiss. Berlin*, **1897**, *69, 137, 487.* **IV.** *J. H. van't Hoff and F. B. Kenrick. Ibid., 508.* **V.** *J. H. van't Hoff and W. Meyerhoffer. Ibid., 1019.* **VI.** *J. H. van't Hoff and F. G. Donnan. Ibid., 1146.* **VII.** *J. H. van't Hoff and T. Estreicher-Rozbierski. Ibid., 487.* **IX.** *J. H. van't Hoff and W. Meyerhoffer. Ibid., 590.* **X.** *J. H. van't Hoff and P. Williams. Ibid., 808.* **XI.** *J. H. van't Hoff and W. Meyerhoffer. Ibid., 814.* — The first two papers of this series treating of the equilibrium between magnesium chlorid and water, have already been reviewed (**3**, 179) from Zeit. phys. Chem. **27**, 75 (1898). The third paper deals with the equilibrium between potassium chlorid and

water, and between potassium chlorid, magnesium chlorid and water. At $-33.6°$ is the cryohydric point with ice, $MgCl_2 12H_2O$ and KCl as solid phases; at 16.7° there is a quintuple point with $MgCl_2 12H_2O$, $MgCl_2 8H_2O$ and KCl as solid phases. Owing to the sparing solubility of potassium chlorid in presence of an excess of magnesium chlorid, the temperatures of these two points do not differ perceptibly from the corresponding temperatures for the system without potassium chlorid. At $-12°$ the solid phases are $MgCl_2 8H_2O$, $MgCl_2 6H_2O$ and KCl. Following up the boundary curve along which carnallite and $MgCl_2 8H_2O$ are solid phases, we find the latter salt changing to the hexahydrate at $-3.4°$ while the hexahydrate is replaced by the tetrahydrate at 116.7°. At 152.5° the carnallite begins to decompose, the solid phases at this quintuple point being $MgCl_2 KCl 6H_2O$, $MgCl_2 4H_2O$ and KCl. Following along the boundary curve with $MgCl_2 KCl 6H_2O$ and KCl as solid phases we reach a maximum temperature at 167.5°. The boundary curve then runs back to lower temperatures terminating at $-12°$ where the octohydrate appears. The field for carnallite has thus been determined. The data are plotted in van't Hoff's usual manner; but it seems a pity that they should not also have been represented in the triangular diagram as this would have brought out much more clearly the significance of the melting-point at 162.5°. As it is the authors made no reference to the theorem of van Rijn van Alkemade. It is interesting to observe that the lower decomposition point for carnallite lies below the lowest temperature at which $MgCl_2 6H_2O$ can exist in equilibrium with solution and vapor. In a final paragraph the authors point out three new ways of converting carnallite into magnesium chlorid and potassium chlorid.

The fourth paper deals with the system, magnesium chlorid, and calcium chlorid and water, especial stress being laid on the conditions of equilibrium for tachhydrite, $Mg_2Cl_4CaCl_2 12H_2O$. At 21.95° there is a quintuple point with $MgCl_2 6H_2O$, $CaCl_2 6H_2O$ and the double salt as solid phases. Below this temperature the double salt cannot exist in equilibrium with solution and vapor. The boundary curve with $MgCl_2 6H_2O$ and the double salt as solid phases ends at 116.7°, at which temperature the hexahydrate of magnesium chlorid changes to the tetrahydrate. The boundary curve with $CaCl_2 6H_2O$ and double salt as solid phases ends at 25°, the hexahydrate of calcium chlorid changing to the tetrahydrate. The upper limits of the field for tachhydrate were not determined but some qualitative measurements showed that the highest temperature at which this compound can exist in pressure of vapor must be about 168°.

The fifth paper is devoted to a consideration of the crystallization phenomena at 25° when the solution contains magnesium chlorid, potassium sulfate, magnesium sulfate and potassium chlorid, the crystals being removed as fast as formed. The salts that can be made to separate at this temperature are KCl, K_2SO_4, $MgCl_2 6H_2O$, $MgSO_4 7H_2O$, $MgSO_4 6H_2O$, $K_2SO_4.MgSO_4 6H_2O$ and $KCl.MgCl_2 6H_2O$. From the solubility phenomena it is shown what may be expected qualitatively and quantitatively, and these deductions are then confirmed both by qualitative and by quantitative crystallizations.

In the sixth paper we find vapor-pressure determinations for the solutions considered in the fifth paper. It is pointed out that when water is removed at

constant temperature, the pressure of the system may fall or may remain constant but cannot rise.

The seventh paper repeats the qualitative work of the fifth with the limitation that all solutions shall be saturated with respect to sodium chlorid. Under these circumstances potassium sulfate can no longer occur as a solid phase. In addition to sodium chlorid the new solid phases that can occur are $K_2Na(SO_4)_2$, $MgSO_4 5H_2O$, $MgSO_4 4H_2O$, Na_2SO_4 and $Na_2SO_4 MgSO_4 4H_2O$. The existence of a double salt of sodium chlorid and sodium sulfate was rendered very improbable. Two specimens of the separated mineral, sulfohalite, which were forwarded from America, proved to be sodium chlorid so that this mineral may well be considered as non-existent.

In the eighth paper are to be found solubility determinations for solutions of magnesium chlorid and sulfate at 25°, the points determined being those at which $MgSO_4 7H_2O$ and $MgSO_4 6H_2O$, $MgSO_4 6H_2O$ and $MgSO_4 5H_2O$, $MgSO_4 5H_2O$ and $MgSO_4 4H_2O$, $MgSO_4 4H_2O$ and $MgCl_2 6H_2O$ are solid phases.

The ninth paper is devoted to a quantitative study of the system taken up in the seventh paper. The tenth paper treats of the conditions of equilibrium for leonite, $K_2SO_4.Mg(SO_4)4H_2O$, a mineral which occurs in the salt deposits, but which was not observed in the crystallization experiments described in the seventh paper. It was found that schönite, $K_2SO_4 MgSO_4 6H_2O$ changes into leonite at 47.5° in presence of potassium sulfate, at 41° in presence of $MgSO_4 7H_2O$ and at 19.9° in presence of $MgSO_4 7H_2O$ and KCl. The reason that leonite was not observed in the preceding experiments is that it shows a great tendency to form supersaturated solutions, and therefore does not separate at all unless especial precautions are taken.

The eleventh paper contains a general discussion of the crystallization phenomena at 25° based on the data of the preceding papers and on some additional solubility determinations. At 27° all solutions containing potassium chlorid together with an excess of sodium chlorid give a mixture of sodium chlorid, magnesium chlorid and $KCl.MgCl_2 6H_2O$ as the final crystallization. At the same temperature all solutions containing potassium chlorid and sodium sulfate together with an excess of sodium chlorid give a mixture of sodium chlorid, potassium chlorid and $K_2Na(SO_4)_2$ as the final crystallization. At the same temperature all solutions containing sodium sulfate and magnesium chlorid together with an excess of sodium chlorid, give a mixture of sodium chlorid, magnesium chlorid, and magnesium sulfate tetrahydrate. Lastly, at 27° all solutions containing magnesium chlorid, potassium chlorid and sodium sulfate, together with an excess of sodium chlorid give a mixture of sodium chlorid, magnesium chlorid, magnesium sulfate tetrahydrate and $KCl.MgCl_2 6H_2O$. The only difference in the behavior at 27° and 25° is that at the lower temperature solutions containing much sodium sulfate and relatively little potassium chlorid together with an excess of sodium chlorid, give a mixture of sodium chlorid, anhydrous sodium sulfate and $K_2Na(SO_4)_2$ as the final crystallization.

W. D. B.

On the cause of the retention and release of gases occluded by the oxides of metals. *T. W. Richards. Am. Chem. Jour.* **20**, 701 (*1898*). — Experiments

were made to determine the amount of gas retained by different oxids when heated at different temperatures. The actual temperatures were estimated by noticing what salts would or would not melt. With copper oxid below 850° a state of equilibrium appears to be reached, while above this temperature practically all of the occluded gas may be expelled if the heating be prolonged sufficiently. With zinc oxid no upper limit was reached but it was found that the amount of gas retained decreases with increasing temperature. It was observed that the oxygen escaped much more readily than the nitrogen with the oxids of copper, zinc and magnesium. To account for this the author assumes a transpiration of oxygen due to continued dissociation and reforming of the oxid in question. In support of this view is the fact that the most stable oxid, that of magnesium, retains the occluded oxygen the most tenaciously while the least stable oxid, that of copper, loses its occluded oxygen the most easily. This hypothesis accounts for the escape of the oxygen but not for the retention of the nitrogen unless one assumes (as the author possibly does) a box-like structure of the copper oxid, the problem then being to get the oxygen out without raising the lid. The reviewer feels certain that it is a mistake, in a discussion of this sort, to ignore the relative concentrations of oxygen and nitrogen in the air. *W. D. B.*

Action of calcium sulfate on some alkaline halids. *A. Ditte. Ann. Chim. Phys.* (7) **14,** *294* (*1898*). — Reviewed (**3,** 180) from Comptes rendus, **126,** 694 (1898).

On some compounds of selenium and tellurium. *R. Metzner. Ann. Chim. Phys.* (7) **15,** *203* (*1898*). — Reviewed (**3,** 420) from Comptes rendus, **127,** 54 (*1898*).

On the combustion of hydrogen mixed with an oxy-gas. *M. Berthelot. Ann. Chim. Phys.* (7) **14,** *167* (*1898*). — If we add to a mixture of hydrogen and sulfur dioxid or of hydrogen and carbon dioxid enough oxygen to convert the whole of the hydrogen into water and ignite the mass, the hydrogen will react with the oxygen and not with the sulfur dioxid or the carbon dioxid. If, instead of adding oxygen, we allow the original mixtures to burn in the air, there will be partial reduction of the sulfur dioxid or of the carbon dioxid, the reduction products being sulfur and hydrogen sulfid in the first case, carbon monoxid in the second. *W. D. B.*

On the chemical equilibria between hydrogen and the oxids of carbon. *M. Berthelot. Ann. Chim. Phys.* (7) **14,** *170* (*1898*). — The author makes the point that it is not proper to speak of an equilibrium between carbon dioxid, hydrogen, carbon monoxid and water at high temperatures because the carbon dioxid is dissociated to a perceptible extent, and the water vapor to a slight extent, at these temperatures, so that oxygen is a factor in determining the final distribution. He also points out that carbon monoxid dissociates below 500° into carbon dioxid and a lower oxid of carbon. It is claimed that people have ignored these two facts when considering this reaction from a theoretical point of view. *W. D. B.*

The action of metals on nitric acid. *P. C. Freer and G. O. Higley. Am. Chem. Jour.* **21,** *377 (1899).* — The following conclusions are reached:

1. Silver, copper, iron and electrolytic hydrogen have nearly the same effect on concentrated nitric acid, nearly pure nitrogen dioxid being evolved.

2. In respect to their action on dilute nitric acid, the order of the metals silver, copper, lead, and iron is that of the potential series.

3. The activity of electrolytic hydrogen depends, in a marked degree, upon the character of the electrode upon whose surface it is liberated.

4. Electrolytic hydrogen in contact with cathodes of copper and of silver, effects reduction of nitric acid in proportion to the current density.

5. When nitric acid having a specific gravity of 1.05 is subjected to electrolysis in cells having cathodes of silver and lead, respectively, on the surface of which cathodes there is equal current density, the reduction products are the same, i. e., nitrogen and ammonia in approximately the same proportions.

6. Silver and lead, when dissolved in acid of specific gravity 1.05, yield reduction products which are widely different, both qualitatively and quantitatively, since from the silver there is obtained nitric oxid and nitrogen dioxid equivalent respectively to ninety-five and five percent of the metal dissolved, while with lead the products are nitric oxid, nitrogen dioxid and nitrous oxid equivalent, in the order named, to 2.5, 7.5 and 70 percent of metal dissolved.

7. Lead reduces nitric acid of specific gravity 1.05 much more completely than copper, yielding about five times more nitrous oxid than the latter. On the other hand copper when made the cathode of an electrolytic cell containing the same strength of acid, has a much greater energizing effect upon the hydrogen deposited upon its surface than is shown by lead under the same circumstances and produces almost three times as much ammonia as the latter. This conclusion is even more emphatically impressed on us by comparison of the results with lead and silver.

8. Since in the electrolysis of nitric acid with a constant current the action of metallic ions is excluded, and the reduction must be effected by the hydrogen ions in contact with the surface of the different metals, and since, therefore, the hydrogen ion, in contact with the respective metals, is the sole reducing agent, it follows that the widely different products obtained when lead and silver dissolve in nitric acid cannot be attributed to the hydrogen atoms alone, but must also involve the direct deoxidizing effect of the metals themselves. Undoubtedly with the concentrated, and hence not ionized, acid, the metals alone cause the change, but with a greater dilution both metals and hydrogen unite in causing reduction. The theory of nascent hydrogen cannot therefore be held in regard to the stronger acids, in which only nitrogen dioxid and nitric oxid are given off, but, subject to the modifications given above, is undoubtedly valid in relation to dilute acid. *W. D. B.*

Action of sulfuric acid on metals. *M. Berthelot. Ann. Chim. Phys.* (7) **14,** *176 (1898).* — Zinc is attacked by sulfuric acid chiefly with evolution of hydrogen. By varying the concentrations and temperatures considerable quantities of sulfur dioxid and hydrogen sulfid may be formed. The sulfurous acid may be further acted upon by zinc and the hydrogen sulfid may be decomposed

by the sulfuric acid. At 145° the action of iron on sulfuric acid forms hydrogen and sulfur dioxid, the escaping gas containing seventy-five percent of sulfur dioxid. With cadmium, sulfur dioxid does not appear much below 160°; with lead, sulfur dioxid is given off at 180°. Mercury is not attacked by cold $H_2SO_4H_2O$. With silver, sulfur dioxid is given off above 100°; the same with copper. At 160° cuprous sulfate is formed. All the metals attack sulfurous acid. *W. D. B.*

Remarks on the reaction between hydrogen and sulfur dioxid, and on the nascent state. *M. Berthelot. Ann. Chim. Phys.* (7) **14,** *289* (*1898*). — A tabulated statement of the conditions under which hydrogen does or does not react with sulfur dioxid, and a recapitulation of the author's theory of nascent hydrogen, published in 1864, in which everything is referred to secondary heat effects. *W. D. B.*

Direct action of sulfuric acid on mercury at ordinary temperatures. *M. Berthelot. Comptes rendus,* **125,** *749* (*1897*); *Ann Chim. Phys.* (7) **13,** *70* (*1898*). — Sulfuric acid of maximum concentration attacks pure mercury in the cold; but this is not the case with a diluted acid. Thermochemical data are cited to explain this. *W. D. B.*

Influence of oxygen on the decomposition of the hydracids by metals and especially by mercury. *M. Berthelot. Ann. Chim. Phys.* (7) **13,** *73* (*1898*).— Reviewed (**3,** 123) from Comptes rendus, **125,** 746 (1897).

On the first stages of the combination between hydrogen and oxygen. *M. Berthelot. Ann. Chim. Phys.* (7) **13,** *30* (*1898*). — Reviewed (**3,** 122) from Comptes rendus, **125,** 171 (1897).

On the analysis of oxygen in gaseous mixtures and on the use of chromous salts. *M. Berthelot. Comptes rendus,* **127,** *24*; *Ann. Chim. Phys.* (7) **15,** *289* (*1898*). — A study of the absorption of oxygen by chromous salts. It was observed that chromous chlorid in presence of concentrated hydrochloric acid decomposes water with evolution of hydrogen. (Cf. Peters, **2,** 452.) *W. D. B.*

On the absorption of oxygen by pyrogallate of potassium. *M. Berthelot. Comptes rendus,* **126,** *1066, 1459*; *Ann. Chim. Phys.* (7) **15,** *294* (*1898*). — One formula weight of pyrogallol absorbs three of oxygen when potassium or sodium hydroxid is present in excess, four with ammonia in excess, and one with barium hydroxid in excess. *W. D. B.*

On the decomposition of nitric acid by heat at moderate temperatures. *M. Berthelot. Comptes rendus,* **127,** *83*; *Ann. Chim. Phys.* (7) **15,** *325* (*1898*). — Nitric acid does not decompose in the dark at ordinary temperatures but does at 100°. The reaction is then discussed on a thermochemical basis. *W. D. B.*

On the reaction between free hydrogen and nitric acid. *M. Berthelot. Comptes rendus,* **127,** *87*; *Ann. Chim. Phys.* (7) **15,** *321* (*1898*). — Free hydrogen does not attack concentrated or dilute nitric acid even at 100°. *W. D. B.*

Action of hydrogen on sulfuric acid. *M. Berthelot. Ann. Chim. Phys.* (7) **13,** *64* (*1898*). — Reviewed (**3,** 123) from Comptes rendus, **125,** 743 (1897).

Velocities.

The inversion of sugar by salts. *L. Kahlenberg, D. J. Davis and R. E. Fowler. Am. Chem. Jour.* **21**, *1* (*1899*). — The authors have studied the action of various sulfates and chlorids on sugar solutions, following the course of the reaction by means of freezing-point determinations when the color of the solutions made the use of the polariscope difficult. At 55.5° the sulfates of manganese, zinc and cadmium had no inverting effect; the sulfates of nickel, copper and aluminum inverted cane sugar, the rate of inversion being highest with the aluminum salt and lowest with the nickel salt. The order for the chlorids is: manganese, cadmium, copper, mercury, aluminum, the aluminum sulfate giving the highest reaction velocity. The authors call attention to the fact that, with the exception of aluminum, this is the order of the electrolytic solution tensions. The fact that chlorids invert more rapidly than sulfates is said to be "because the ionizing tendency of chlorin is greater than that of the sulfuric radical". *W. D. B.*

The decomposition of sulphonic ethers by water, acids and salts. *J. H. Kastle, P. Murrill, and J. C. Frazer. Am. Chem. Jour.* **19**, *894* (*1897*). — One one-thousandth formula weight of the ethyl ether of *p*-brombenzenesulfonic acid was dissolved in fifty formula weights of acetone and fifty thousandths formula of a weight of water or alcohol were added. Under these conditions the concentration of the water or the alcohol may be considered as remaining constant and the reaction becomes a monomolecular one. A satisfactory constant was obtained, the reaction running nearly four times as fast with water as with alcohol. The presence of the acids and salts apparently decreased the reaction velocity but it was found that two reactions were then taking place simultaneously:

$$RSO_2C_2H_5 + MX = RSO_2OM + C_2H_5X$$
$$RSO_2C_2H_5 + HOH = RSO_2OH + C_2H_5OH.$$

On changing the method of analysis so as to keep track of both reactions it was found that the rate of decomposition was higher with acids than with water. *W. D. B.*

On the hydrolysis of acid amids. *J. Remsen and E. E. Reid. Am. Chem. Jour.* **21**, *281* (*1899*). — The authors have determined the rate of hydrolysis of ortho-, meta- and para-nitrobenzamids with hydrochloric and sulfuric acids, the rate of hydrolysis of the same amids with alkalies, and the rate of hydrolysis of seventeen amids with hydrochloric acid at the temperature of boiling water. The reaction is bimolecular even in alkaline solutions and satisfactory constants were obtained in nearly every case. The presence of neutral salts has a marked effect. The effect of temperature changes may be expressed by the formula $\partial \log K / \partial T = B$. The ortho substituted benzamids react much less readily than the others, and the nature of the substituted group appears to be of more importance than its formula weight. *W. D. B.*

The oxidation of formic aldehyde by hydrogen peroxide. *J. H. Kastle and A. S. Loevenhart. Jour. Am. Chem. Soc.* **21**, *262* (*1899*). — A study of the rate of oxidation of formaldehyde by hydrogen peroxide. The reaction proved

to be bimolecular. At 20° the reaction runs more rapidly in the light than in the dark; at about 90° the rates are the same. It seems probable that the reaction runs with almost infinite slowness below zero both in direct sunlight and in the dark. Acids accelerate the reaction somewhat and bases enormously. It is therefore proposed to use this reaction as a means of determining the amount of hydrolysis in salts of weak acids. *W. D. B.*

Comparative study of the three dinitrobenzenes. II. *C. A. Lobry de Bruyn and A. Steger. Recueil Trav. Pays-Bas*, **18**, *9* (*1899*). — Menschutkin assumed that in all reactions involving disubstituted benzene compounds either the meta or the para compound would show the intermediate reaction velocity, but never the ortho compound. In the reaction between the dinitrobenzenes and sodium alcoholates the authors have found an instance in which the para compound reacts with the greatest and the meta compound with the least velocity. It is also pointed out that a similar phenomenon was noticed years ago by Post and Mertens in the reaction of aqueous solutions of the nitrophenols on barium carbonate. *W. D. B.*

The rate of substitution of a nitro group in ortho- and paradinitrobenzene by an alcoholate. *A. Steger. Recueil Trav. Pays-Bas*, **18**, *13* (*1899*). — The author worked with sodium methylate in methyl alcohol solution and with sodium ethylate in ethyl alcohol solution. The reaction with sodium methylate may be represented by the equation

$$C_6H_4(NO_2)_2 + NaOCH_3 = C_6H_3NO_2.OCH_3 + NaNO_2.$$

The reaction velocity is higher with *p*-dinitrobenzene than with *o*-dinitrobenzene, and higher with sodium ethylate than with sodium methylate. The reaction velocity practically doubles for a rise of ten degrees in temperature, the rate of change being a trifle greater with *p*-dinitrobenzene than with *o*-dinitrobenzene. The *p*-dinitrobenzene reacts eight to nine times as fast with sodium ethylate as does the *o*-dinitrobenzene, and two and one-half to three and one-half times as fast with sodium methylate. The reaction velocity constant is independent of the absolute and relative concentrations, and is not affected by the presence of the sodium salt whereas the constants in the formation of ethers from alkyl iodids and sodium alcoholates (Conrad, Hecht and Brückner) increased with increasing dilution and decreased on addition of sodium iodid. *W. D. B.*

Studies on the influence of the medium on the reaction velocity of gaseous systems. *E. Cohen. Zeit. phys. Chem.* **25**, *483* (*1898*). — The decomposition of arsin was taken as the reaction to be studied. It was found that the rate of decomposition at 310° was not affected by the presence of hydrogen or of nitrogen. On the other hand a change in the surface of the glass may cut the reaction velocity down ninety percent. *W. D. B.*

On the influence of temperature and certain metallic oxids on the formation of sodium sulfate from sulfur dioxid, air and sodium chlorid. *J. Krutzwig and A Dernoncourt. Recueil Trav. Pays-Bas*, **17**, *348* (*1898*). — A continuation of the work described in a previous paper (**2**, 204) with special reference to the effect of temperature. It was found that at constant temperature the change of

sodium chlorid into sulfate is accelerated by increasing the amount of ferric oxid. When the temperature alone changes, the maximum yield is obtained at about 500°. Copper oxid is a much better catalytic agent than ferric oxid and is most efficient at about 450°. *W. D. B.*

New experiments on the explosive properties of acetylene. *M. Bethelot and Vieille. Ann. Chim. Phys.* (7) **13**, *1* (*1898*). — Reviewed (**1**, 749) from Comptes rendus, **124**, 988, 996, 1000 (1897).

Electromotive Forces.

Studies on metallic sulfid electrodes. *I. Bernfeld. Zeit. phys. Chem.* **25**, *46* (*1898*). — The reaction at the lead sulfid electrode may be represented by the equation $PbS + H_2S \rightleftarrows Pb + 2\overline{HS}$, and the formula for the concentration cell is

$$\pi = \frac{RT}{E} \log \frac{C'_{HS}}{C_{HS}} - \frac{RT}{2E} \log \frac{C_1'_{H_2S}}{C_{1H_2S}}$$

where the C′ and C_1' refer to the more concentrated solution. By keeping the partial pressure of hydrogen sulfid gas the same in the two solutions the second term on the right-hand side of the equation drops out and it is possible to study the effects due to variations in the concentrations of sodium sulfhydrid, the current flowing through the cell from the more to the less concentrated solution. By keeping the concentration of sodium sulfhydrate the same in the two solutions, the first term on the right-hand side of the equation drops out and it is possible to study the effect of varying the partial pressures of hydrogen sulfid, the current now running through the cell from the more dilute to the more concentrated solution. Both these things were tried and a satisfactory quantitative agreement between experiment and theory was obtained. Experiments were also made with silver sulfid and with bismuth sulfid as electrodes. *W. D. B.*

On a new (fourth) kind of inversion cell. *E. Cohen. Zeit. phys. Chem.* **25**, *300* (*1898*). — The new form of cell has one electrode reversible with respect to the cation and the other reversible with respect to the anion, the two electrodes dipping into a saturated solution of a salt, the stable solid salt being present. The Clark cell with saturated zinc sulfate solution belongs under this head. If we determine and plot the corresponding temperatures and electromotive forces, we shall find a break in the curve at the temperature at which $ZnSO_4 7H_2O$ changes into $ZnSO_4 6H_2O$. From the measurements of Callendar and Barnes the author finds 38.75° for the inversion temperature. From the solubility determinations of Callendar and Barnes the point appears to lie at 39.90°, while the author's measurements with the dilatometer place the point at 38.50°. *W. D. B.*

A contribution to the theory of the lead accumulator. *F. Foerster. Zeit. Elektrochemie*, **3**, *525* (*1897*). — The author prefers LeBlanc's hypothesis of tetravalent, lead as ion to Liebenow's hypothesis of bivalent lead peroxid as ion, because the former view harmonizes better with the phenomena observed in the electrolysis of solutions of copper and of thallium salts. *W. D. B.*

On the electromotive behavior of chromium. *W. Hittorf. Sitzungsber. Akad. Wiss. Berlin*, **1898**, *193. Reviewed* (**2**, *450*) *from Zeit. phys. Chem.* **25**, *729* (*1898*).

On the use of aluminum for changing alternating into direct currents. *A Campetti. Atti. Accad. Sci. Torino*, **34**, *90* (*1898*). — Experiments have been made to determine the loss of energy when an alternating current is transformed into a direct one by means of aluminum anodes and platinum cathodes, the electrolyte being potash alum. The alternating current was obtained from storage cells by means of a rotating commutator. It was found that the efficiency is greater, the higher the current density at the electrodes; but it is probable that the minimum waste always exceeds the five percent estimated by Graetz. A solution of chrome alum was much less satisfactory than one of potash alum.

W. D. B.

Addition to the paper: On the residual current observed with polarized electrodes. *E. Salomon. Zeit. phys. Chem.* **25**, *365* (*1898*). — In the original paper (**2**, 66) it was postulated that "a stationary state will occur when the amount of metal transported by the current in a given time is equal to the amount of metal carried in the opposite direction by diffusion". This is not right because the two forces work in the same direction. A new and presumably more accurate formula is worked out which does not agree at all with the experimental data, whereas the old formula represented these data very satisfactorily. No explanation could be found to account for this dicrepancy.

W. D. B.

Determination of the internal resistance of galvanic cells having low polarization capacities. *E. Haagn. Zeit. Elektrochemie*, **3**, *440* (*1897*). — Reviewed (**1**, 697) from Zeit. phys. Chem. **23**, 97 (1897).

Principles of construction, and efficiency of our mirror galvanometers. *T. Des Coudres. Zeit. Elektrochemie*, **3**, *417*, *441*, *465*, *489*, *513* (*1897*). — A most serviceable and interesting account of the general principles of the Wiedemann, Thomson, and Deprez-d'Arsonval types of galvanometer. *W. D. B.*

Absolute electrometer for small differences of potential. *A. Pérot and C. Fabry. Ann. Chim. Phys.* (*7*) **13**, *404* (*1898*). — The complete description of the instrument, a brief account of which has already been published (**1**, 520).

Electrolysis and Electrolytic Dissociation.

The electrolysis of mixtures. *A Schrader. Zeit. Elektrochemie*, **3**, *498* (*1897*). — The author has determined the transference numbers of mixtures of potassium chlorid and potassium iodid, of sulfuric acid and copper sulfate. Assuming that the migration velocities are the same in the mixtures as in the solutions of the single salts, the author calculates the amount of dissociation in the mixtures. He also compares the amount of copper precipitated secondarily from the acid copper sulfate solution with the amount that would have been precipitated secondarily, if no hydrogen had been set free. *W. D. B.*

On current distribution in mixed solutions of electrolytes. *K. Hopfgartner. Zeit. phys. Chem.* **25**, *115*; *Zeit. Elektrochemie*, **4**, *445* (*1898*). — The transfer-

ence number N_{Cl} for hydrochloric acid varies irregularly about a mean value of 0.167 as the concentration changes from $n/10$ to $9n/10$. The corresponding value N_{Cl} for sodium chlorid increases from 0.617 to 0.635 through the same range of concentrations, and the value N_{Cl} for barium chlorid rises from 0.579 to 0.617. For N_{SO_4} in $CuSO_4$ there was found 0.696 for normal solutions and 0.684 for two-thirds normal solutions. Experiments were then made to determine the transference numbers in different mixtures of sodium chlorid and hydrochloric acid, of barium chlorid and hydrochloric acid, and of copper and magnesium sulfates. The general conclusion reached was that the transference numbers remain unchanged in mixtures at any rate up to moderate concentrations. *W. D. B.*

Electrolytic reduction of nitrobenzene. *W. Löb. Zeit. Elektrochemie*, **3**, *471* (*1897*). — In formic acid, acetic acid or oxalic acid solution with lead cathodes, the chief reduction product was benzidin, the yield being 70–80 percent of the theoretical. In ammoniacal solution azobenzene was formed together with some hydrazobenzene. *W. D. B.*

Contributions to the electrolysis of the alkaline bromids and fluorids. *H. Pauli. Zeit. Elektrochemie*, **3**, *474* (*1897*). — With potassium bromid the results were like those obtained by Oettel with potassium chlorid, save that the bromate was more easily reduced than the chlorate, and that it was not possible to obtain bromate alone with but the merest trace of hypobromite. When potassium fluorid was electrolyzed there was evolution of ozone and the glass was etched but neither oxyfluorid nor hydrogen peroxid could be detected. *W. D. B.*

On the copper voltameter. *F. Foerster. Zeit. Elektrochemie*, **3**, *479* (*1897*). — Reviewed (**1**, 525) from Zeit. anorg Chem. **14**, 106 (1897).

On the influence of the time on the process at the cathode in the electrolysis of copper sulfate solution. *C. Ullmann. Zeit. Elektrochemie*, **3**, *516* (*1897*). — The author worked with horizontal electrodes and constant current, and noted the time between the closing of the circuit and the sudden increase of polarization which always precedes the precipitation of black copper and the evolution of gas. It was found that $i_1 \sqrt{t}/m = const$ where i = current, t = time and m = concentration. The value of the constant appears to increase slightly as the value of m decreases. *W. D. B.*

The LeSueur process for the electrolytic production of sodium hydroxide and chlorine. *C. L. Parsons. Jour. Am. Chem. Soc.* **20**, *868* (*1898*). — An account of the process for making caustic soda and bleaching powder now in use at Rumford Falls. *W. D. B.*

The formation of alums by electrolysis. *J. L. Howe and E. A. O'Neal. Jour. Am. Chem. Soc.* **20**, *759* (*1898*). — Iron ammonium alum can easily be obtained in quantity by electrolyzing a solution of ferrous sulfate, ammonium sulfate and sulfuric acid between platinum electrodes. A current of about 0.02 amperes was used. Iron rubidium alum and iron cesium alum were prepared in a similar manner substituting rubidium sulfate and cesium sulfate respectively for ammonium sulfate. The authors also prepared cobalt rubidium, cobalt cesium

and chromium ammonium alums but were unsuccessful in their attempts to make various manganese alums. The electrolysis of cesium ruthenium nitrosochlorid plus sulfuric acid yielded ruthenium teroxid. *W. D. B.*

Measurements of the electrical conductivity of dilute solutions at temperatures up to 100°. *R. Schaller. Zeit. phys. Chem.* **25,** *497* (*1898*). — It was found that the electrodes hold traces of solution fast, and that they must be washed a long time before they can be used with water. It is therefore desirable to use as small electrodes as possible. Vessels made of Jena glass can be used for neutral salts and acids even at 99°. With electrolytes which may be considered as completely dissociated the conductivity was found to be practically a linear function of the temperature. The conductivity of partly dissociated acids increases more and more slowly as the temperature rises and may pass through a maximum. The degree of dissociation of these substances decreases with rising temperature. The temperature coefficients of sodium salts with the same number of combining weights in the anion are equal. The substances studied were KCl, NaCl, KNO_3, $NaNO_3$, HCl, NaOH ; the sodium salts of benzoic, salicylic, *m*-toluylic, cinnamic, anisic, *p*-toluylic, *o*-toluylic, *p*-nitrobenzoic, *o*-nitrobenzoic, *m*-nitrobenzoic, *o*-chlorbenzoic, *o*-iodbenzoic, *o*-brombenzoic and *m*-brombenzoic acids; the free acids with the exception of *p*-nitrobenzoic, *o*-brombenzoic and *m*-brombenzoic acids, and including *m*-iodbenzoic acid and α-bromcinnamic acid. *W. D. B.*

On the successive dissociations of dibasic organic acids. *W. A. Smith. Zeit. phys. Chem.* **25.** *144, 93* (*1898*). — The concentration of hydrogen as ion was calculated from the rates at which the acids and the acid salts invert cane sugar at 100°. It was noticed that potassium chlorid inverts sugar at 100°. The following general conclusions were reached. The dissociation of the second hydrogen as ion is less and the dissociation of the first hydrogen as ion is greater the nearer together the two carboxyl groups are. The dissociation of the second hydrogen as ion is less in a substituted than in the original acid save when the substituting group is hydroxyl. The influence of the substituting groups has the opposite effect on the dissociation of the second hydrogen as ion from that which it has on the dissociation of the first hydrogen as ion. *W. D. B.*

Metathetic reactions between certain salts in solution in liquid ammonia. *E. C. Franklin and C. A. Kraus. Am. Chem. Jour.* **21,** *1* (*1899*). — The authors have dissolved the nitrates of lithium, sodium, potassium, calcium, strontium, barium, magnesium, zinc, manganese, cobalt, nickel, cadmium, mercury, lead, silver, and copper in liquid ammonia and have added to these solutions of the sulfid, chlorid, bromid, iodid, chromate and borate of ammoniun in the same solvent. Owing to the dissociating power of liquid ammonia, it was believed that metathetical reactions would take place promptly when the reaction products were insoluble. This proved to be the case and the results are presented in tabular form. *W. D. B.*

Dielectricity and Optics.

On the refraction of air, oxygen, nitrogen, argon, hydrogen and helium. *W. Ramsey and M. W. Travers. Zeit. phys. Chem.* **25,** *100* (*1898*). — The method was that of Rayleigh. Taking the index of refraction of air as unity, the fol-

lowing values were found: hydrogen, 0.4733; oxygen, 0.9243; nitrogen, 1.0163; argon, 0.9596; carbon dioxid, 1.5316. It was found that the index of refraction of air is a little higher than that calculated from the values for the component gases while for a mixture of hydrogen and helium the found value was about three percent lower than the calculated value. *W. D. B.*

On the refraction and dispersion of silicon in its compounds. *G. Abati. Zeit. phys. Chem.* **25,** *353 (1898).* — Data are tabulated for eleven compounds of silicon. The atomic refraction of silicon as calculated from the compounds varies not only with the constitution and the type of the compound, but with the nature of the elements, becoming larger as the substituting group changes from alcoholate through chlorin and bromin to an alkyl group. The value obtained from the propyl orthosilicate is 7.58; from hexapropyldisilicate, 6.04. This lower value is believed to be due to the presence of the group Si-O-Si. The specific dispersion increases from chlorid to bromid and has the highest value with silicon ethyl. The general results remain unchanged whether the n or the n^2 formula be used for calculating the specific refraction. *W. D. B.*

The color of sulphur vapor. *J. L. Howe and S. G. Hamner. Jour. Am. Chem. Soc.* **20,** *757 (1898).* — "The color of sulphur vapor varies with the temperature, being of an orange tint just above its boiling-point, deepening to a red which is strongest at 500°, and then becoming lighter with increasing temperature. The color at the boiling-point is that of a normal solution of potassium bichromate; that of the deepest red is that of a rather dilute solution of ferric thiocyanate." *W. D. B.*

On the color of compounds of bromin and iodin. *J. H. Kastle. Am. Chem. Jour.* **21,** *398 (1899).* — A dilute aqueous solution of bromin has practically the same color as chlorin water. The author attributes the yellow and red colors of some bromids and iodids to the presence of the free bromin and free iodin. The change of some bromids and iodids from white to yellow or red on heating is due to the increase of dissociation with rise of temperature. The author has made a strong argument in favor of his hypothesis and it now remains to be seen how useful this hypothesis is to be. *W. D. B.*

On the realization of an optically empty liquid. *W. Spring. Bull. Acad. roy. Belg.* **1899,** *174; Recueil Trav. Pays-Bas,* **18,** *153 (1899).* — Tyndall called a gas optically empty when the path of a ray of light could not be detected. In 1869 Lallemand showed that all liquids became illuminated when a ray of light passed through them. Since then it has been a disputed question whether this irradiation were due to particles in suspension or were an inherent property of liquids. Spring has confirmed the previous observations that it is impossible to make liquid optically empty by distillation. Filtration through cotton-wool increased the irradiation. On the other hand passing an electric current of high potential through the solution, or forming a colloidal precipitate and allowing it to settle gave an optically empty liquid. *W. D. B.*

On the reason for the absence of color in certain limpid, natural waters. *W. Spring. Recueil Trav. Pays-Bas,* **17,** *359 (1898).* — Pure water has a blue color. If the complementary color be added, the result will be a colorless liquid. The author shows that the presence of haematite in a moderately thick

layer on the bottom of the pond, lake or river will produce this effect as will also invisible particles of the same substance in suspension. *W. D. B.*

On the single cause of the blue color of water. *W. Spring. Bull. Acad. roy. Belg.* **1899,** *72; Recueil Trav. Pays-Bas,* **18,** 1 (*1899*). — Tyndall's experiments have been repeated and it was found that suspended particles do not give a blue color to the water. Further experiments showed that fluorescence was not a factor, and the final conclusion reached is that the blue color of water is due simply and solely to the fact that water is blue in color. *W. D. B.*

Experiments on the relations subsisting between light and chemical energy. *M. Berthelot. Comptes rendus,* **127,** *143; Ann. Chim. Phys.* (*7*) **15,** (*1898*). — Nitric, iodic, and hydriodic acids are decomposed by sunlight at ordinary temperatures, the reaction products being the same as when these substances are decomposed by heat. The rays from the blue end of the spectrum are the most efficacious, the decomposition of nitric acid being entirely prevented by the interposition of a solution of potassium bichromate. Red mercuric oxid is more readily decomposed by light than the yellow oxid. *W. D. B.*

Observations on the action of oxygen on carbon bisulfid, and on the chemical action of light. *M. Berthelot. Comptes rendus,* **126,** *1060; Ann. Chim. Phys.* (*7*) **14,** *155* (*1898*). — A flask containing carbon bisulfid and air was left for a year in a well-lighted room where it, however, received no direct sunlight. At the end of that time, no change could be detected. A similar flask was exposed to direct sunlight and decomposition of the carbon bisulfid was found to have taken place. From this the author concludes that the reaction between carbon bisulfid and oxygen requires a certain intensity of light to start it, differing in this respect from the reaction between hydrogen and chlorin. *W. D. B.*

On the decomposition of some substances under the influence of electrical oscillations. *A. v. Hemptinne. Zeit. phys. Chem.* **25,** *284* (*1898*). — The substances are all decomposed by electrical oscillations. Isomeric substances sometimes gave the same and sometimes different reaction products. The alcohols, aldehydes, acetones, acids and ethers which do not contain more than one or two of oxygen and which have a relatively simple constitution decompose in such a way as to form a hydrocarbon and oxygen, carbon monoxid or carbon dioxid. Thus the chief reaction products of acetone are carbon monoxid and a mixture of ethane and methane. No generalizations could be made as to the way benzene compounds decompose. (See **1,** 630). *W. D. B.*

The effect of X-rays on the luminosity of gases. *A. v. Hemptinne. Zeit. phys. Chem.* **26,** *165* (*1898*). — Gases and vapors become luminous at distinctly higher pressures when acted on simultaneously by the X-rays and by electrical oscillations alone. The percentage rise of pressure is 32.4 for hydrogen, 33.3 for oxygen, 57.1 for methyl alcohol, 57.5 for ethyl alcohol, 64.3 for ether and 80 for chloroform. (See **1,** 630). *W. D. B.*

On the series spectra of oxygen, sulphur and selenium. *C. Runge and F. Paschen. Astrophys. Jour.* **8,** *70* (*1898*). — This is the full paper an abstract of which has already been reviewed. (**2,** 271).

Crystallography, Capillarity and Viscosity.

The surface tensions of aqueous solutions of alkaline chlorides. *C. E. Linebarger. Jour. Am. Chem. Soc.* **21**, *411* (*1899*). — The author has determined the surface tensions of aqueous solutions of lithium, sodium and potassium chlorids at 25°. The measurements run to saturated solutions with sodium and potassium chlorids, and nearly to saturation with lithium chlorid. The surface tension increases with increasing concentration and is not a linear function of the concentration, though the variation from the straight line is very slight for moderate ranges of concentration. When the concentrations are expressed in formula weights per liter the curves for the three salts are identical.

W. D. B.

Viscosity of supercooled liquids. *G. Tammann. Zeit. phys. Chem.* **28**, *17* (*1899*). — When a substance is called solid or liquid, its greater or less viscosity is usually considered as the criterion. This leads to contradictions and is not a suitable standard. A discontinuity in the rate of change of at least some of the properties of the substance at the point of passing from the liquid to the solid condition of aggregation is the only definition always applicable. Crystalline bodies show such discontinuity without exception; even the fluid crystals show it. Amorphous bodies do not. Therefore all amorphous bodies are to be considered as snpercooled liquids. Thus solid is synonymous with crystallized. Measurements of the viscosity of substances have not been carried very far because of the ease with which spontaneous crystallization takes place. Some substances are now known which do not crystallize readily and the investigations may be carried out. The viscosity of a liquid may be calculated from the rate at which a sphere falls through it. Experiments were undertaken, determining the rate at which a small platinum sphere one millimeter in diameter, fell through piperin and betol at different temperatures. The recovery of the ball for the next experiment took too long, so another method was adopted. A glass rod was hung in the liquid to be investigated by a thread passing over a wheel, and a small excess weight at the other side imparted an inclination to rise to the rod. The rate was measured at which the rod rose through the substance at different temperatures. Experiments were carried out with piperin, betol, alphol, peucedamin, cocain, papaverin, grape sugar, brucin and cane sugar. On the average the rod began to move perceptibly 90° below the melting-points of the substances. The viscosity diminishes so rapidly with increasing temperature that it may be said no other property of substances changes at such a rate. No point of discontinuity was observed in its rate of change. Experiments were made on the change in volume and in the surface tension of betol with increasing temperature. No break was perceptible in the continuous change of these properties.

S. L. B.

Measure of the coefficient of viscosity of air. *C. Fabry and A. Pérot. Ann. Chim. Phys.* (*7*) **13**, *275* (*1898*). — The electrometer previously described (**1**, 520) reaches the position of equilibrium very slowly when the distance between the plates is small, because of the viscosity of the film of air. A study of the movement caused by a small excess charge in the centre of the movable plate has led to a new measure of the coefficient of viscosity of air. The final value is $\eta = 1.73 \times 10^{-4}$ dynes/cm^2.

W. D. B.

THERMAL COEFFICIENTS

BY J. E. TREVOR

Introduction

In the thermodynamics of isotropic one-phase systems of constant mass and composition, it has long been known that the thermal coefficients Y_1 and Y_2 of the heat equation

$$d'Q = Y_1 dx_1 + Y_2 dx_2,$$

in which x_1 and x_2 represent the independent state-variables of the system, can be expressed as functions of certain fundamental functions — the energy, the 'characteristic functions' of Massieu, and the χ-function of Gibbs — and the partial derivatives of these functions. A few of these formulas are well known. The object of the present paper is to derive them all, and to point out the analytical relationship that obtains between them.

If we take the volume v and the thermal potential, the thermodynamic temperature, θ of our system as independently variable, the pressure p and the entropy η will be determined by these quantities; and we shall have two equations

$$f(p, v, \theta) = 0 \qquad (1)$$

$$\phi(\eta, v, \theta) = 0, \qquad (2)$$

of unknown forms, between these four variables, and such that by elimination we may obtain the two further equations

$$F(p, \theta, \eta) = 0 \qquad (3)$$

$$\Phi(p, v, \eta) = 0. \qquad (4)$$

Because of these four equations, we may use the equations

$$\left.\begin{aligned}
\frac{\partial p}{\partial v}\frac{\partial v}{\partial \theta}\frac{\partial \theta}{\partial p} &= -1 \\
\frac{\partial \eta}{\partial v}\frac{\partial v}{\partial \theta}\frac{\partial \theta}{\partial \eta} &= -1 \\
\frac{\partial p}{\partial \theta}\frac{\partial \theta}{\partial \eta}\frac{\partial \eta}{\partial p} &= -1 \\
\frac{\partial p}{\partial v}\frac{\partial v}{\partial \eta}\frac{\partial \eta}{\partial p} &= -1,
\end{aligned}\right\} \tag{5}$$

which correspond to them.

We have, further, for the differential of the energy of the system,

$$d\mathbf{E} = -pdv + \theta d\eta;$$

wherefore, with the aid of the definitions

$$\mathbf{F} = \mathbf{E} - \theta\eta \tag{6}$$
$$\mathbf{G} = \mathbf{E} + pv \tag{7}$$
$$\mathbf{H} = \mathbf{E} + pv - \theta\eta, \tag{8}$$

we can write the familiar differential equations

$$d\mathbf{E}(v,\eta) = -pdv + \theta d\eta \tag{9}$$
$$d\mathbf{F}(v,\theta) = -pdv - \eta d\theta \tag{10}$$
$$d\mathbf{G}(p,\eta) = vdp + \theta d\eta \tag{11}$$
$$d\mathbf{H}(p,\theta) = vdp - \eta d\theta, \tag{12}$$

from which follow, successively, the four 'thermodynamic relations'

$$\frac{\partial p}{\partial \eta} = -\frac{\partial \theta}{\partial v} \tag{13}$$
$$\frac{\partial p}{\partial \theta} = \frac{\partial \eta}{\partial v} \tag{14}$$
$$\frac{\partial v}{\partial \eta} = \frac{\partial \theta}{\partial p} \tag{15}$$
$$-\frac{\partial v}{\partial \theta} = \frac{\partial \eta}{\partial p}. \tag{16}$$

All these relations can be derived directly from (9), by changing

the independent variables. To them, further, by this means, can be added, in p and v, the so-called 'fifth thermodynamic relation'

$$\frac{\partial \eta}{\partial v}\frac{\partial \theta}{\partial p} - \frac{\partial \eta}{\partial p}\frac{\partial \theta}{\partial v} = 1, \tag{17}$$

and a similar equation in θ and η.

Now, because of (2), (3), and (4), we can write the heat equation of our system in the forms

$$\theta d\eta = B_\theta\, dv + C_v\, d\theta \tag{18}$$
$$= A_\theta\, dp + C_p\, d\theta \tag{19}$$
$$= B_p\, dv + A_v\, dp, \tag{20}$$

in which equations the thermal coefficients A, B, C correspond in turn to the variables p, v, θ. This notation has marked advantages over that commonly employed. These equations define the thermal coefficients

$$A_v(v, p) \qquad A_\theta(p, \theta)$$
$$B_p(v, p) \qquad B_\theta(v, \theta)$$
$$C_v(v, \theta) \qquad C_p(p, \theta).$$

Expressing each of the equations (18), (19), (20) in the three different sets of independent variables, we have:

In v,θ: $$\theta d\eta = B_\theta\, dv + C_v\, d\theta \tag{18a}$$

" p,θ: $$= B_\theta \frac{\partial v}{\partial p}\, dp + \left(B_\theta \frac{\partial v}{\partial \theta} + C_v\right) d\theta \tag{18b}$$

" v,p: $$= \left(B_\theta + C_v \frac{\partial \theta}{\partial v}\right) dv + C_v \frac{\partial \theta}{\partial p}\, dp; \tag{18c}$$

In p,θ: $$\theta d\eta = A_\theta\, dp + C_p\, d\theta \tag{19a}$$

" v,θ: $$= A_\theta \frac{\partial p}{\partial v}\, dv + \left(A_\theta \frac{\partial p}{\partial \theta} + C_p\right) d\theta \tag{19b}$$

" v,p: $$= C_p \frac{\partial \theta}{\partial v}\, dv + \left(C_p \frac{\partial \theta}{\partial p} + A_\theta\right) dp; \tag{19c}$$

In v,p : $$\theta d\eta = B_p\, dv + A_v\, dp \tag{20a}$$

" v,θ : $$= \left(B_p + A_v \frac{\partial p}{\partial v}\right) dv + A_v \frac{\partial p}{\partial \theta} d\theta \tag{20b}$$

" p,θ : $$= \left(B_p \frac{\partial v}{\partial p} + A_v\right) dp + B_p \frac{\partial v}{\partial \theta} \partial\theta. \tag{20c}$$

Comparing, now, the different pairs of equations in the same variables, and rearranging, we find the following six relations between the six thermal coefficients :

$$\left\{\begin{aligned} B_\theta &= A_\theta \frac{\partial p}{\partial v} && (21)\\ &= B_p + A_v \frac{\partial p}{\partial v} && (22)\end{aligned}\right.$$

$$\left\{\begin{aligned} B_p &= C_p \frac{\partial \theta}{\partial v} && (23)\\ &= B_\theta + C_v \frac{\partial \theta}{\partial v} && (24)\end{aligned}\right.$$

$$\left\{\begin{aligned} C_v &= A_v \frac{\partial p}{\partial \theta} && (25)\\ &= A_\theta \frac{\partial p}{\partial \theta} + C_p. && (26)\end{aligned}\right.$$

It should be noted that the above derivation of these relations (21) to (26) is essentially as follows. Solving equations (2), (3), and (4) for η; and substituting successively, in each one, the value of each of the independent variables, as taken from the equation of state (1); we get the series of equations

$$\begin{aligned} \eta &= g[v, \theta(p,v)] & \eta &= h[v(p,\theta), \theta]\\ &= i[p, \theta(p,v)] & &= j[p(v,\theta), \theta]\\ &= k[p, v(p,\theta)] & &= l[p(v,\theta), v]. \end{aligned}$$

Differentiating these equations with respect to each of the independent variables in turn, we find

$$\begin{cases} \left(\dfrac{\partial \eta}{\partial v}\right)_p = \left(\dfrac{\partial \eta}{\partial v}\right)_\theta + \left(\dfrac{\partial \eta}{\partial \theta}\right)_v \dfrac{\partial \theta}{\partial v} \\ \left(\dfrac{\partial \eta}{\partial p}\right)_v = \left(\dfrac{\partial \eta}{\partial \theta}\right)_v \dfrac{\partial \theta}{\partial p}, \end{cases}$$

and so on through the set. These equations, when multiplied through by θ, become the relations (21) to (26).

Direct determinations

From the heat equations (18), (19), (20),

$$\theta d\eta = \mathrm{B}_\theta\, dv + \mathrm{C}_v\, d\theta \tag{18}$$

$$= \mathrm{A}_\theta\, dp + \mathrm{C}_p\, d\theta \tag{19}$$

$$= \mathrm{B}_p\, dv + \mathrm{A}_v\, dp, \tag{20}$$

we deduce for the thermal coefficients the formulas

$$\mathrm{A}_v = \theta\left(\frac{\partial \eta}{\partial p}\right)_v \tag{27}$$

$$\mathrm{A}_\theta = \theta\left(\frac{\partial \eta}{\partial p}\right)_\theta \tag{28}$$

$$\mathrm{B}_p = \theta\left(\frac{\partial \eta}{\partial v}\right)_p \tag{29}$$

$$\mathrm{B}_\theta = \theta\left(\frac{\partial \eta}{\partial v}\right)_\theta \tag{30}$$

$$\mathrm{C}_v = \theta\left(\frac{\partial \eta}{\partial \theta}\right)_v \tag{31}$$

$$\mathrm{C}_p = \theta\left(\frac{\partial \eta}{\partial \theta}\right)_p. \tag{32}$$

Each of the fundamental functions **E**, **F**, **G**, **H**, by means of which these several thermal coefficients are to be expressed, contains two independent variables, say x and y. In the case of the energy these variables are v and η. Now, in any case, the indicated derivatives in certain of the equations (27) to (32) exhibit these variables, and a dependent variable z. In the first equation of the set, for example, we find the independent variables

x,η of the energy equation, and a dependent variable p. In these indicated derivatives, both or but one of the new independent variables may occur within the parentheses: in some cases we shall have

$$\left(\frac{\partial z}{\partial x}\right)_y \quad \text{or} \quad \left(\frac{\partial x}{\partial z}\right)_y,$$

in others

$$\left(\frac{\partial x}{\partial y}\right)_z \quad \text{or} \quad \left(\frac{\partial y}{\partial x}\right)_z.$$

In the first of these cases we have, for the thermal coefficient,

$$\mathrm{Y} = \theta\left(\frac{\partial z}{\partial x}\right)_y,$$

or

$$\mathrm{Y} = \frac{\theta}{\left(\frac{\partial z}{\partial x}\right)_y},$$

either of which reduces to the desired result on effecting the differentiation of the dependent variable z, and replacing θ by its value, when θ is not one of the independent variables.

In the second case, when we have

$$\mathrm{Y} = \theta\left(\frac{\partial x}{\partial y}\right)_z \quad \text{or} \quad \mathrm{Y} = \theta\left(\frac{\partial y}{\partial x}\right)_z,$$

we find the expression for the thermal coefficient, by eliminating the indicated derivative between the equation in question and the general relation (5),

$$\frac{\partial x}{\partial y}\,\frac{\partial y}{\partial z}\,\frac{\partial z}{\partial x} = -1,$$

which may also be written

$$\frac{\partial y}{\partial x}\,\frac{\partial x}{\partial z}\,\frac{\partial z}{\partial y} = -1,$$

whereby we find

$$\mathbf{Y} = -\frac{(\partial z/\partial y)_x}{(\partial z/\partial x)_y}$$

or

$$\mathbf{Y} = -\frac{(\partial z/\partial x)_y}{(\partial z/\partial y)_x}.$$

This result is then reduced as before.

When neither of these cases occurs, when only one of the variables to be employed appears in the indicated derivative, it may happen that this derivative is related, through one of the four thermodynamic relations, with a derivative in which both x and y do appear. In this event, the original derivative may be replaced by the new one, and the reduction be continued as before. In these ways we shall obtain the thermal coefficients in sets of four, as functions of the different fundamental functions and their partial derivatives. The remaining two in each case must then be found with the aid of the relations (21) to (26) between the coefficients.

The energy, E

The energy, **E**, is a function of v and η. The equations of the set (27) to (32) that exhibit these variables are

$$\begin{cases} \mathbf{A}_v = \theta\left(\dfrac{\partial \eta}{\partial p}\right)_v \\ \mathbf{C}_v = \theta\left(\dfrac{\partial \eta}{\partial \theta}\right)_v \\ \mathbf{B}_p = \theta\left(\dfrac{\partial \eta}{\partial v}\right)_p \\ \mathbf{B}_\theta = \theta\left(\dfrac{\partial \eta}{\partial v}\right)_\theta. \end{cases}$$

Taking them in order, we have, first,

$$\mathbf{A}_v = \theta\left(\frac{\partial \eta}{\partial p}\right)_v = \frac{\theta}{(\partial p/\partial \eta)_v},$$

or, because of (9),

$$A_v = \frac{\dfrac{\partial \mathbf{E}}{\partial \eta}}{\dfrac{\partial^2 \mathbf{E}}{\partial v \partial \eta}}. \tag{33}$$

Second, we have

$$C_v = \theta \left(\frac{\partial \eta}{\partial \theta}\right)_v$$

$$= \frac{\theta}{(\partial \theta / \partial \eta)_v},$$

whence, because of (9),

$$C_v = \frac{\dfrac{\partial \mathbf{E}}{\partial \eta}}{\dfrac{\partial^2 \mathbf{E}}{\partial \eta^2}}. \tag{34}$$

Third, we have

$$B_p = \theta \left(\frac{\partial \eta}{\partial v}\right)_p;$$

or, from the relation (5) in η, v, p,

$$\frac{\partial \eta}{\partial v} \frac{\partial v}{\partial p} \frac{\partial p}{\partial \eta} = -1, \tag{5}$$

$$B_p = -\theta \frac{(\partial p / \partial v)_\eta}{(\partial p / \partial \eta)_v},$$

whence, because of (9),

$$B_p = -\frac{\partial \mathbf{E}}{\partial \eta} \cdot \frac{\dfrac{\partial^2 \mathbf{E}}{\partial v^2}}{\dfrac{\partial^2 \mathbf{E}}{\partial v \partial \eta}}. \tag{35}$$

Fourth, we have

$$B^\theta = \theta \left(\frac{\partial \eta}{\partial v}\right)_\theta;$$

or, from the relation (5) in η, v, θ,

(5) $$\frac{\partial\eta}{\partial v}\,\frac{\partial v}{\partial\theta}\,\frac{\partial\theta}{\partial\eta} = -1,$$

$$B_\theta = -\theta\frac{(\partial\theta/\partial v)_\eta}{(\partial\theta/\partial\eta)_v},$$

whence, because of (9),

$$B_\theta = -\frac{\partial\mathbf{E}}{\partial\eta}\cdot\frac{\dfrac{\partial^2\mathbf{E}}{\partial\eta\partial v}}{\dfrac{\partial^2\mathbf{E}}{\partial\eta^2}}. \qquad (36)$$

This leaves A_θ and C_p to be found with the aid of the relations (21) to (26) between the coefficients.

The free energy, F

The free energy, **F**, is a function of v and θ. The equations of the set (27) to (32) that exhibit these variables are

$$\begin{cases} B_\theta = \theta\left(\dfrac{\partial\eta}{\partial v}\right)_\theta \\ C_v = \theta\left(\dfrac{\partial\eta}{\partial\theta}\right)_v \\ A_v = \theta\left(\dfrac{\partial\eta}{\partial p}\right)_v, \text{ with } \left(\dfrac{\partial p}{\partial\eta}\right)_v = -\left(\dfrac{\partial\theta}{\partial v}\right)_\eta \\ A_\theta = \theta\left(\dfrac{\partial\eta}{\partial p}\right)_\theta, \text{ with } \left(\dfrac{\partial\eta}{\partial p}\right)_\theta = -\left(\dfrac{\partial v}{\partial\theta}\right)_p. \end{cases}$$

First, we have

$$B_\theta = \theta\left(\frac{\partial\eta}{\partial v}\right)_\theta,$$

or, because of (10),

$$B_\theta = -\theta\frac{\partial^2\mathbf{F}}{\partial v\partial\theta}. \qquad (37)$$

Second, we have

$$C_v = \theta\left(\frac{\partial\eta}{\partial\theta}\right)_v,$$

or, because of (10),

$$C_v = -\theta \frac{\partial^2 \mathbf{F}}{\partial \theta^2}. \tag{38}$$

Third, we have

$$A_v = \theta \left(\frac{\partial \eta}{\partial p}\right)_v,$$

or, by the first thermodynamic relation (13),

$$A_v = -\theta \left(\frac{\partial v'}{\partial \theta}\right)_\eta,$$

or, from the relation (5) in v', θ, η,

$$\frac{\partial v'}{\partial \theta}\frac{\partial \theta}{\partial \eta}\frac{\partial \eta}{\partial v'} = -1, \tag{5}$$

$$A_v = \theta \frac{(\partial \eta/\partial \theta)_v}{(\partial \eta/\partial v')_\theta};$$

whence, because of (10),

$$A_v = \theta \frac{\dfrac{\partial^2 \mathbf{F}}{\partial \theta^2}}{\dfrac{\partial^2 \mathbf{F}}{\partial \theta \partial v'}}. \tag{39}$$

Fourth, we have

$$A_\theta = \theta \left(\frac{\partial \eta}{\partial p}\right)_\theta,$$

or, by the fourth thermodynamic relation (16),

$$A_\theta = -\theta \left(\frac{\partial v}{\partial \theta}\right)_p,$$

or, from the relation (5) in v, θ, p,

$$\frac{\partial v'}{\partial \theta}\frac{\partial \theta}{\partial p}\frac{\partial p}{\partial v'} = -1, \tag{5}$$

$$A_\theta = \theta \frac{(\partial p/\partial \theta)_v}{(\partial p/\partial v')_\theta},$$

whence, because of (10),

$$A_\theta = \theta \frac{\dfrac{\partial^2 \mathbf{F}}{\partial v \partial \theta}}{\dfrac{\partial^2 \mathbf{F}}{\partial v^2}}. \tag{40}$$

This leaves B_p and C_p to be found with the aid of the relations (21) to (26) between the coefficients.

The heat function, G

The heat function, **G**, is a function of p and η. The equations of the set (27) to (32) that exhibit these variables are

$$\begin{cases} B_p = \theta \left(\dfrac{\partial \eta}{\partial v}\right)_p \\ C_p = \theta \left(\dfrac{\partial \eta}{\partial \theta}\right)_p \\ A_v = \theta \left(\dfrac{\partial \eta}{\partial p}\right)_v \\ A_\theta = \theta \left(\dfrac{\partial \eta}{\partial p}\right)_\theta. \end{cases}$$

First, we have

$$B_p = \theta \left(\frac{\partial \eta}{\partial v}\right)_p$$

$$= \frac{\theta}{(\partial v/\partial \eta)_p},$$

or, because of (11),

$$B_p = \frac{\dfrac{\partial \mathbf{G}}{\partial \eta}}{\dfrac{\partial^2 \mathbf{G}}{\partial p \partial \eta}}. \tag{41}$$

Second, we have

$$C = \theta \left(\frac{\partial \eta}{\partial \theta}\right)_p$$

$$= \frac{\theta}{(\partial \theta/\partial \eta)_p},$$

or, because of (11),

$$C_p = \frac{\dfrac{\partial G}{\partial \eta}}{\dfrac{\partial^2 G}{\partial \eta^2}}. \tag{42}$$

Third, we have

$$A_v = \theta \left(\frac{\partial \eta}{\partial p}\right)_v;$$

or, from the relation (5) in η, p, v,

$$\frac{\partial \eta}{\partial p}\,\frac{\partial p}{\partial v}\,\frac{\partial v}{\partial \eta} = -1, \tag{5}$$

$$A_v = -\theta \frac{(\partial v/\partial p)_\eta}{(\partial v/\partial \eta)_p},$$

whence, because of (11),

$$A_v = -\frac{\partial G}{\partial \eta} \cdot \frac{\dfrac{\partial^2 G}{\partial p^2}}{\dfrac{\partial^2 G}{\partial p \partial \eta}}. \tag{43}$$

Fourth, we have

$$A_\theta = \theta \left(\frac{\partial \eta}{\partial p}\right)_\theta;$$

or, from the relation (5) in η, p, θ,

$$\frac{\partial \eta}{\partial p}\,\frac{\partial p}{\partial \theta}\,\frac{\partial \theta}{\partial \eta} = -1, \tag{5}$$

$$A_\theta = -\theta \frac{(\partial \theta/\partial p)_\eta}{(\partial \theta/\partial \eta)_p},$$

whence, because of (11),

$$A_\theta = -\frac{\partial G}{\partial \eta} \cdot \frac{\dfrac{\partial^2 G}{\partial p \partial \eta}}{\dfrac{\partial^2 G}{\partial \eta^2}}. \tag{44}$$

This leaves B_θ and C_v to be found with the aid of the relations (21) to (26) between the coefficients.

The thermodynamic potential, H

The thermodynamic potential, **H**, is a function of p and θ. The equations of the set (27) to (32) that exhibit these variables are

$$\begin{cases} A_\theta = \theta \left(\dfrac{\partial \eta}{\partial p}\right)_\theta \\ C_p = \theta \left(\dfrac{\partial \eta}{\partial \theta}\right)_p \\ B_p = \theta \left(\dfrac{\partial \eta}{\partial v'}\right)_p, \quad \text{with} \quad \left(\dfrac{\partial v'}{\partial \eta}\right)_p = \left(\dfrac{\partial \theta}{\partial p}\right)_\eta \\ B_\theta = \theta \left(\dfrac{\partial \eta}{\partial v'}\right)_\theta, \quad \text{with} \quad \left(\dfrac{\partial \eta}{\partial v'}\right)_\theta = \left(\dfrac{\partial p}{\partial \theta}\right)_v. \end{cases}$$

First, we have

$$A_\theta = \theta \left(\frac{\partial \eta}{\partial p}\right)_\theta,$$

or, because of (12),

$$A_\theta = -\theta \frac{\partial^2 \mathbf{H}}{\partial p \partial \theta}. \tag{45}$$

Second, we have

$$C_p = \theta \left(\frac{\partial \eta}{\partial \theta}\right)_p,$$

or, because of (12),

$$C_p = -\theta \frac{\partial^2 \mathbf{H}}{\partial \theta^2}. \tag{46}$$

Third, we have

$$B_p = \theta \left(\frac{\partial \eta}{\partial v'}\right)_p,$$

or, by the third thermodynamic relation, (15),

$$B_p = \theta \left(\frac{\partial p}{\partial \theta}\right)_\eta,$$

or, from the relation (5) in p, θ, η,

$$\frac{\partial p}{\partial \theta}\,\frac{\partial \theta}{\partial \eta}\,\frac{\partial \eta}{\partial p} = -1,$$

$$B_p = -\theta \frac{(\partial \eta/\partial \theta)_p}{(\partial \eta/\partial p)_\theta},$$

whence, because of (12),

$$B_p = -\theta \frac{\dfrac{\partial^2 \mathbf{H}}{\partial \theta^2}}{\dfrac{\partial^2 \mathbf{H}}{\partial p \partial \theta}}. \tag{47}$$

Fourth, we have

$$B_\theta = \theta \left(\frac{\partial \eta}{\partial v}\right)_\theta,$$

or, by the second thermodynamic relation (14),

$$B_\theta = \theta \left(\frac{\partial p}{\partial \theta}\right)_v,$$

or, from the relation (5) in p,θ,v,

$$\frac{\partial p}{\partial \theta}\,\frac{\partial \theta}{\partial v}\,\frac{\partial v}{\partial p} = -1,$$

$$B_\theta = -\theta \frac{(\partial v/\partial \theta)_p}{(\partial v/\partial p)_\theta},$$

whence, because of (12),

$$B_\theta = -\theta \frac{\dfrac{\partial^2 \mathbf{H}}{\partial p \partial \theta}}{\dfrac{\partial^2 \mathbf{H}}{\partial p^2}}. \tag{48}$$

This leaves A_v and C_v to be found with the aid of the relations (21) to (26) between the coefficients.

The undetermined coefficients

The problem. — Under each of the four fundamental functions, two thermal coefficients remain to be expressed in terms of the function and its derivatives. These coefficients, together with the equation — of the set (21) to (26) — with the aid of

which the first coefficient of each pair may be so expressed, are exhibited in the following table.

THE UNDETERMINED COEFFICIENTS

Function	Coefficient	Relation	
E	A_θ	$A_\theta = B_\theta \left(\frac{\partial v'}{\partial p}\right)_\theta$	(21)
	C_p		
F	B_p	$B_p = B_\theta + C_v \left(\frac{\partial \theta}{\partial v'}\right)_p$	(24)
	C_p		
G	B_θ	$B_\theta = A_\theta \left(\frac{\partial p}{\partial v'}\right)_\theta$	(21)
	C_v		
H	A_v	$A_v = A_\theta + C_p \left(\frac{\partial \theta}{\partial p}\right)_v$.	(25–26)
	C_v		

The energy. — First, we have A_θ given by the relation (21),

$$A_\theta = B_\theta \left(\frac{\partial v'}{\partial p}\right)_\theta. \tag{21}$$

To pass to the variables v and η we must note that, in v, p, θ,

$$\frac{\partial v'}{\partial p}\,\frac{\partial p}{\partial \theta}\,\frac{\partial \theta}{\partial v'} = -1, \tag{5}$$

wherefore

$$A_\theta = -B_\theta \frac{(\partial\theta/\partial p)_v}{(\partial\theta/\partial v')_p};$$

which value is transformed by the fifth thermodynamic relation (17),

$$\frac{\partial \eta}{\partial v'}\,\frac{\partial \theta}{\partial p} - \frac{\partial \eta}{\partial p}\,\frac{\partial \theta}{\partial v'} = 1, \tag{17}$$

to

$$A_\theta = -B_\theta \left(\frac{\left(\frac{\partial \eta}{\partial p}\right)_v}{\left(\frac{\partial \eta}{\partial v'}\right)_p} + \frac{1}{\left(\frac{\partial \eta}{\partial v'}\right)_p \left(\frac{\partial \theta}{\partial v'}\right)_p} \right),$$

in which v' and η appear in all the indicated derivatives save $(\partial\theta/\partial v')_p$. By (24) we have

$$\left(\frac{\partial\theta}{\partial v'}\right)_p = \frac{B_p - B_\theta}{C_v},$$

whence

$$A_\theta = -B_\theta\left(\frac{\left(\frac{\partial\eta}{\partial p}\right)_v}{\left(\frac{\partial\eta}{\partial v'}\right)_p} + \frac{C_v}{(B_p - B_\theta)\left(\frac{\partial\eta}{\partial v'}\right)_p}\right).$$

Reducing this equation in the same way as before, we find

$$A_\theta = \frac{\frac{\partial E}{\partial\eta}\cdot\frac{\partial^2 E}{\partial v'\partial\eta}}{\frac{\partial^2 E}{\partial v'^2}\frac{\partial^2 E}{\partial\eta^2} - \left(\frac{\partial^2 E}{\partial v'\partial\eta}\right)^2}. \tag{49}$$

The remaining coefficient, C_p, must be found through one of the relations (21) to (26). But since all these relations exhibit only p, v', and θ, and none of them the pair of variables v', η, we must select from the set a relation that contains C_p and a derivative that is related to one in v', η through a 'thermodynamic relation.' The only such thermodynamic relation is the second,

(14) $$\frac{\partial p}{\partial\theta} = \frac{\partial\eta}{\partial v'};$$

and the only relation that contains both C_p and $\partial p/\partial\theta$ is (26),

(26) $$C_v = A_\theta\left(\frac{\partial p}{\partial\theta}\right)_v + C_p$$

$$= A_\theta\left(\frac{\partial\eta}{\partial v'}\right)_\theta + C_p.$$

Since, now,

(5) $$\frac{\partial\eta}{\partial v'}\frac{\partial v'}{\partial\theta}\cdot\frac{\partial\theta}{\partial\eta} = -1,$$

we have

$$C_p = C_v + A_\theta\frac{(\partial\theta/\partial v')_\eta}{(\partial\theta/\partial\eta)_v},$$

which reduces to

$$C_p = \frac{\dfrac{\partial E}{\partial \eta} \cdot \dfrac{\partial^2 E}{\partial v^2}}{\dfrac{\partial^2 E}{\partial v^2}\dfrac{\partial^2 E}{\partial \eta^2} - \left(\dfrac{\partial^2 E}{\partial v \partial \eta}\right)^2}. \tag{50}$$

The free energy. — The coefficient B_p is given by the relation (24),

$$B_p = B_\theta + C_v \left(\frac{\partial \theta}{\partial v}\right)_p; \tag{24}$$

or, from (5) in θ, v, p,

$$\frac{\partial \theta}{\partial v}\frac{\partial v}{\partial p}\frac{\partial p}{\partial \theta} = -1, \tag{5}$$

$$B_p = B_\theta - C_v \frac{(\partial p/\partial v)_\theta}{(\partial p/\partial \theta)_v}.$$

Reducing, as before, we find

$$B_p = \theta \frac{\dfrac{\partial^2 F}{\partial v^2}\dfrac{\partial^2 F}{\partial \theta^2} - \left(\dfrac{\partial^2 F}{\partial v \partial \theta}\right)^2}{\dfrac{\partial^2 F}{\partial v \partial \theta}}. \tag{51}$$

The remaining coefficient, C_p, is given by (23),

$$C_p = B_p \left(\frac{\partial v}{\partial \theta}\right)_p; \tag{23}$$

or, from (5) in v, θ, p,

$$\frac{\partial v}{\partial \theta}\frac{\partial \theta}{\partial p}\frac{\partial p}{\partial v} = -1, \tag{5}$$

$$C_p = -B_p \frac{(\partial p/\partial \theta)_v}{(\partial p/\partial v)_\theta},$$

which reduces to

$$C_p = -\theta \frac{\dfrac{\partial^2 F}{\partial v^2}\dfrac{\partial^2 F}{\partial \theta^2} - \left(\dfrac{\partial^2 F}{\partial v \partial \theta}\right)^2}{\dfrac{\partial^2 F}{\partial v^2}}. \tag{52}$$

The heat function. — The coefficient B_θ is given by the relation (21),

$$B_\theta = A^\theta \left(\frac{\partial p}{\partial v}\right)_\theta. \tag{21}$$

To pass to the variables p,η we must note that, in p, v, θ,

$$\frac{\partial p}{\partial v}\frac{\partial v}{\partial \theta}\frac{\partial \theta}{\partial p} = -1, \tag{5}$$

wherefore,

$$B_\theta = -A_\theta \frac{(\partial\theta/\partial v)_p}{(\partial\theta/\partial p)_v};$$

which value is transformed by the fifth thermodynamic relation (17),

$$\frac{\partial \eta}{\partial v}\frac{\partial \theta}{\partial p} - \frac{\partial \eta}{\partial p}\frac{\partial \theta}{\partial v} = 1, \tag{17}$$

to

$$B_\theta = -A_\theta\left(\frac{\left(\frac{\partial \eta}{\partial v}\right)_p}{\left(\frac{\partial \eta}{\partial p}\right)_v} - \frac{1}{\left(\frac{\partial \theta}{\partial p}\right)_v\left(\frac{\partial \eta}{\partial p}\right)_v}\right),$$

in which p and η appear in all the indicated derivatives save $(\partial\theta/\partial p)_v$. By (25) and (26) we have

$$\left(\frac{\partial \theta}{\partial p}\right)_v = \frac{A_v - A_\theta}{C_p},$$

whence

$$B_\theta = -A_\theta\left(\frac{\left(\frac{\partial \eta}{\partial v}\right)_p}{\left(\frac{\partial \eta}{\partial p}\right)_v} - \frac{C_p}{(A_v - A_\theta)\left(\frac{\partial \eta}{\partial p}\right)_v}\right).$$

Reducing, as before, we find

$$B_\theta = \frac{-\frac{\partial G}{\partial \eta}\cdot\frac{\partial^2 G}{\partial p \partial \eta}}{\frac{\partial^2 G}{\partial p^2}\frac{\partial^2 G}{\partial \eta^2} - \left(\frac{\partial^2 G}{\partial p \partial \eta}\right)^2}. \tag{53}$$

The remaining coefficient, C_v, must be found through one

of the relations (21) to (26). But since all these relations exhibit only p, v, and θ, and none of them the pair of variables p,η, we must select from the set a relation that contains C_p and a derivative that is related to one in p,η through a 'thermodynamic relation.' The only such thermodynamic relation is the fourth,

$$\frac{\partial v}{\partial \theta} = -\frac{\partial \eta}{\partial p}; \tag{16}$$

and the only relation that contains both C_v and $\partial v/\partial\theta$ is, from (23) and (24),

$$C_p = B_\theta \left(\frac{\partial v}{\partial \theta}\right)_p + C_v$$

$$= -B_\theta \frac{\partial \eta}{\partial p} + C_v.$$

Since, now,

$$\frac{\partial \eta}{\partial p}\,\frac{\partial p}{\partial \theta}\,\frac{\partial \theta}{\partial \eta} = -1, \tag{5}$$

we have

$$C_v = C_p - B_\theta \frac{(\partial\theta/\partial p)_\eta}{(\partial\theta/\partial\eta)_p},$$

which reduces to

$$C_v = \frac{\dfrac{\partial G}{\partial \eta}\cdot\dfrac{\partial^2 G}{\partial p^2}}{\dfrac{\partial^2 G}{\partial p^2}\,\dfrac{\partial^2 G}{\partial \eta^2} - \left(\dfrac{\partial^2 G}{\partial p\,\partial \eta}\right)^2}. \tag{54}$$

The thermodynamic potential. — The coefficient A_v is given by the relations (25) and (26) as

$$A_v = A_\theta + C_p \left(\frac{\partial \theta}{\partial p}\right)_v;$$

or, from (5) in θ, p, v,

$$\frac{\partial \theta}{\partial p}\,\frac{\partial p}{\partial v}\,\frac{\partial v}{\partial \theta} = -1, \tag{5}$$

$$A_v = A_\theta - C_p \frac{(\partial v/\partial p)_\theta}{(\partial v/\partial\theta)_p}.$$

Reducing, as before, we find

$$A_v = \theta \frac{\frac{\partial^2 H}{\partial p^2}\frac{\partial^2 H}{\partial \theta^2} - \left(\frac{\partial^2 H}{\partial p \partial \theta}\right)^2}{\frac{\partial^2 H}{\partial p \partial \theta}}. \tag{55}$$

The remaining coefficient, C_v, is given by (25),

(25) $$C_v = A_v \left(\frac{\partial p}{\partial \theta}\right)_v;$$

or, from (5) in p, θ, v,

(5) $$\frac{\partial p}{\partial \theta}\frac{\partial \theta}{\partial v}\frac{\partial v}{\partial p} = -1,$$

$$C_v = -A_v \frac{(\partial v/\partial \theta)_p}{(\partial v/\partial p)},$$

which reduces to

$$C_v = -\theta \frac{\frac{\partial^2 H}{\partial p^2}\frac{\partial^2 H}{\partial \theta^2} - \left(\frac{\partial^2 H}{\partial p \partial \theta}\right)^2}{\frac{\partial^2 H}{\partial p^2}}. \tag{56}$$

The results

We have now expressed each of our thermal coefficients

$$A_v \quad A_\theta \quad B_p \quad B^\theta \quad C_v \quad C_p$$

as a function of each of the fundamental functions **E**, **F**, **G**, **H** and its derivatives. The resulting equations fall naturally into three sets, of eight each, in the following order:

SET I.

v, θ independent,	$C_v = -\theta \frac{\partial^2 F}{\partial \theta^2}$	(38)
" "	$B_\theta = -\theta \frac{\partial^2 F}{\partial v \partial \theta}$	(37)
p, θ "	$C_p = -\theta \frac{\partial^2 H}{\partial \theta^2}$	(46)

p,θ *independent*	$A_\theta = -\theta \dfrac{\partial^2 H}{\partial p \partial \theta}$	(45)
v,η "	$C_v = \dfrac{\dfrac{\partial H}{\partial \eta}}{\dfrac{\partial^2 H}{\partial \eta^2}}$	(34)
" "	$A_v = \dfrac{\dfrac{\partial H}{\partial \eta}}{\dfrac{\partial^2 E}{\partial v \partial \eta}}$	(33)
p,η "	$C_p = \dfrac{\dfrac{\partial G}{\partial \eta}}{\dfrac{\partial^2 G}{\partial \eta^2}}$	(42)
" "	$B_p = \dfrac{\dfrac{\partial G}{\partial \eta}}{\dfrac{\partial^2 G}{\partial p \partial \eta}}$	(41)

SET II.

v,θ *independent*,	$A_v = \theta \dfrac{\dfrac{\partial^2 H}{\partial \theta^2}}{\dfrac{\partial^2 F}{\partial v \partial \theta}}$	(39)
" "	$A_\theta = \theta \dfrac{\dfrac{\partial^2 F}{\partial v \partial \theta}}{\dfrac{\partial^2 F}{\partial v^2}}$	(40)
p,θ "	$B_p = -\theta \dfrac{\dfrac{\partial^2 H}{\partial \theta^2}}{\dfrac{\partial^2 H}{\partial p \partial \theta}}$	(47)

p,θ *independent*, $$B_\theta = -\theta \frac{\frac{\partial^2 H}{\partial p \partial \theta}}{\frac{\partial^2 H}{\partial p^2}} \qquad (48)$$

v,η *independent* $$B_p = -\frac{\partial E}{\partial \eta} \cdot \frac{\frac{\partial^2 E}{\partial v^2}}{\frac{\partial^2 E}{\partial v \partial \eta}} \qquad (35)$$

" " $$B_\theta = -\frac{\partial E}{\partial \eta} \cdot \frac{\frac{\partial^2 E}{\partial v \partial \eta}}{\frac{\partial^2 E}{\partial \eta^2}} \qquad (36)$$

p,η " $$A_v = -\frac{\partial G}{\partial \eta} \cdot \frac{\frac{\partial^2 G}{\partial p^2}}{\frac{\partial^2 G}{\partial p \partial \eta}} \qquad (43)$$

" " $$A_\theta = -\frac{\partial G}{\partial \eta} \cdot \frac{\frac{\partial^2 G}{\partial p \partial \eta}}{\frac{\partial^2 G}{\partial \eta^2}} . \qquad (44)$$

SET III.

v,θ *independent*, $$C_p = -\theta \frac{\frac{\partial^2 F}{\partial v^2}\frac{\partial^2 F}{\partial \theta^2} - \left(\frac{\partial^2 F}{\partial v \partial \theta}\right)^2}{\frac{\partial^2 F}{\partial v^2}} \qquad (52)$$

" " $$B_p = \theta \frac{\frac{\partial^2 F}{\partial v^2}\frac{\partial^2 F}{\partial \theta^2} - \left(\frac{\partial^2 F}{\partial v \partial \theta}\right)^2}{\frac{\partial^2 F}{\partial v \partial \theta}} \qquad (51)$$

p,θ *independent* $$C_v = -\theta \frac{\frac{\partial^2 H}{\partial p^2}\frac{\partial^2 H}{\partial \theta^2} - \left(\frac{\partial^2 H}{\partial p \partial \theta}\right)^2}{\frac{\partial^2 H}{\partial p^2}} \qquad (56)$$

" " $$A_v = \theta \frac{\frac{\partial^2 H}{\partial p^2}\frac{\partial^2 H}{\partial \theta^2} - \left(\frac{\partial^2 H}{\partial p \partial \theta}\right)^2}{\frac{\partial^2 H}{\partial p \partial \theta}} \qquad (55)$$

v,η " $$C_p = \frac{\frac{\partial E}{\partial \eta}\cdot\frac{\partial^2 E}{\partial v^2}}{\frac{\partial^2 E}{\partial v^2}\frac{\partial^2 E}{\partial \eta^2} - \left(\frac{\partial^2 E}{\partial v \partial \eta}\right)^2} \qquad (50)$$

" " $$A^\theta = \frac{\frac{\partial E}{\partial \eta}\cdot\frac{\partial^2 E}{\partial v \partial \eta}}{\frac{\partial^2 E}{\partial v^2}\frac{\partial^2 E}{\partial \eta^2} - \left(\frac{\partial^2 E}{\partial v \partial \eta}\right)^2} \qquad (49)$$

p,η " $$C_v = \frac{\frac{\partial G}{\partial \eta}\cdot\frac{\partial^2 G}{\partial p^2}}{\frac{\partial^2 G}{\partial p^2}\frac{\partial^2 G}{\partial \eta^2} - \left(\frac{\partial^2 G}{\partial p \partial \eta}\right)^2} \qquad (54)$$

" " $$B_\theta = -\frac{\frac{\partial G}{\partial \eta}\cdot\frac{\partial^2 G}{\partial p \partial \eta}}{\frac{\partial^2 G}{\partial p^2}\frac{\partial^2 G}{\partial \eta^2} - \left(\frac{\partial^2 G}{\partial p \partial \eta}\right)^2}. \qquad (53)$$

As has been obvious in the derivation of these equations, two of each type fall under the head of each fundamental function. Six of the equations, namely numbers (37), (38), (45), (46), (52), and (56), have long been known. A curious feature of the results is the appearance, in the last set of eight, of the Hessians of the fundamental functions. Representing the successive Hessians by H_e, H_f, H_g, H_h, this set may be written in the interesting form:

$$\frac{C_f}{\theta} = \frac{\partial^2 E/\partial v^2}{H_e} \qquad \frac{C_p}{\theta} = \frac{-H_f}{\partial^2 F/\partial v^2}$$

$$\frac{A_\theta}{\theta} = \frac{\partial^2 E/\partial v \partial \eta}{H_e} \qquad \frac{B_p}{\theta} = \frac{H_f}{\partial^2 F/\partial v \partial \theta}$$

$$\frac{C_v}{\theta} = \frac{\partial^2 G/\partial p^2}{H_g} \qquad \frac{C_v}{\theta} = \frac{-H_h}{\partial^2 H/\partial p^2}$$

$$\frac{B_\theta}{\theta} = -\frac{\partial^2 G/\partial p \partial \eta}{H_g} \qquad \frac{A_v}{\theta} = \frac{H_h}{\partial^2 H/\partial p \partial \theta}.$$

Dynamic coefficients

Corresponding to the heat equation

$$\theta d\eta = \theta \frac{\partial \eta}{\partial x_1} + \theta \frac{\partial \eta}{\partial x_2},$$

in its three forms (18), (19), (20), the work equation

$$-p dv = -p \frac{\partial v}{\partial x_1} - p \frac{\partial v}{\partial x_2}$$

assumes the forms

$$\begin{aligned} -p dv &= I_\eta dp + K_p d\eta \\ &= I_\theta dp + J_p d\theta \\ &= J_\eta d\theta + K_\theta d\eta. \end{aligned}$$

These equations serve to define the dynamic coefficients I, J, K, which correspond in order to the variables, p,θ,η. Expressed in terms of the derivatives of the fundamental functions, these dynamic coefficients obviously will assume forms wholly analogous to those found above for the corresponding thermal coefficients.

The total result in both cases amounts simply to the expression, in terms of the derivatives of the fundamental functions, of all the possible derivatives of the entropy,

$$\left(\frac{\partial \eta}{\partial p}\right)_v \quad \left(\frac{\partial \eta}{\partial p}\right)_\theta \quad \left(\frac{\partial \eta}{\partial \theta}\right)_p \quad \left(\frac{\partial \eta}{\partial \theta}\right)_v \quad \left(\frac{\partial \eta}{\partial v}\right)_p \quad \left(\frac{\partial \eta}{\partial v}\right)_\theta,$$

and of the volume,

$$\left(\frac{\partial v}{\partial p}\right)_\theta \quad \left(\frac{\partial v}{\partial p}\right)_\eta \quad \left(\frac{\partial v}{\partial \theta}\right)_p \quad \left(\frac{\partial v}{\partial \theta}\right)_\eta \quad \left(\frac{\partial v}{\partial \eta}\right)_p \quad \left(\frac{\partial v}{\partial \eta}\right)_\theta,$$

each differentiated with respect to each of the other variables in the set p,v,θ,η, and the former multiplied in each case by θ, the latter by $-p$. To complete the set of all the possible derivatives of the quantities p,v,θ,η, each differentiated with respect to each of the others, there remains only to add the derivatives

$$\left(\frac{\partial p}{\partial \theta}\right)_v \quad \left(\frac{\partial p}{\partial \theta}\right)_\eta,$$

or, indeed, their reciprocals.

Cornell University, August, 1899.

ON THE THEOREMS OF ROBIN AND OF MOUTIER

BY PAUL SAUREL

The total thermodynamic potential Φ of a system containing n components in r phases is given by the equation

$$\Phi = \sum_{i=1}^{r} \sum_{j=1}^{n} F_{ij} M_{ij},$$

in which M_{ij} denotes the mass of the j-th component contained in the i-th phase, and F_{ij} is the partial derivative of the potential with respect to that mass. If the system is in equilibrium at the temperature T and under the pressure Π, the volume V and the entropy H are given by the equations

$$V = \frac{\partial \Phi}{\partial \Pi} = \sum_{i=1}^{r} \sum_{j=1}^{n} \frac{\partial F_{ij}}{\partial \Pi} M_{ij},$$

$$-H = \frac{\partial \Phi}{\partial T} = \sum_{i=1}^{r} \sum_{j=1}^{n} \frac{\partial F_{ij}}{\partial T} M_{ij};$$

and for any virtual change in the masses

$$\sum_{i=1}^{r} \sum_{j=1}^{n} F_{ij} \delta M_{ij} = 0.$$

Accordingly, for any virtual change in the system we have

$$\delta\Phi = \delta\Pi \sum_{i=1}^{r} \sum_{j=1}^{n} \frac{\partial F_{ij}}{\partial \Pi} M_{ij} + \delta T \sum_{i=1}^{r} \sum_{j=1}^{n} \frac{\partial F_{ij}}{\partial T} M_{ij} + \sum_{i=1}^{r} \sum_{j=1}^{n} F_{ij} \delta M_{ij}$$
$$= V\delta\Pi - H\delta T.$$

Let us apply this equation to a univariant system. At a given temperature and under the corresponding pressure such a system admits of a continuous series of states of equilibrium for

which the potential has the same value, but for which the volume and the entropy are different. Denoting any two of these states by the subscripts 1 and 2, we shall have

$$\Phi_1 = \Phi_2,$$
$$\delta\Phi_1 = V_1\delta\Pi - H_1\delta T,$$
$$\delta\Phi_2 = V_2\delta\Pi - H_2\delta T.$$

If V_2 is greater than V_1, and if we consider a virtual change in which T remains constant, we shall have

$$\delta\Phi_2 > \delta\Phi_1.$$

That is to say, if we consider at the temperature T and under the pressure $\Pi + \delta\Pi$ two states of the system which are states of equilibrium at the temperature T and under the pressure Π, then the state with the greater volume has the greater potential. But if a system is not in equilibrium at a given temperature and under a given pressure it undergoes a transformation which causes the potential to decrease. Accordingly, if we consider at the temperature T and under the pressure $\Pi + \delta\Pi$ a univariant system in a state which is a state of equilibrium for the temperature T and the pressure Π, the system will undergo a change which, if it occurred at the temperature T and under the equilibrium pressure Π, would be accompanied by a decrease in volume. Similarly, at a pressure slightly less than the equilibrium pressure, the transformation is such that at the equilibrium pressure it would be accompanied by an increase in volume. This is Robin's Theorem.[1]

Next consider a virtual change in which Π remains constant, and let us suppose that H_1 is greater than H_2. Then, the equations under discussion give

$$\delta\Phi_2 > \delta\Phi_1.$$

That is to say, if we consider under the pressure Π and at the temperature $T + \delta T$ two states of the system which are states of equilibrium under the pressure Π and at the temperature T,

[1] Robin. Bulletin de la Société philomathique, (7) 4, 24 (1879). Duhem. Mécanique Chimique, Vol. I., p. 158.

then the state with the smaller entropy has the greater potential. Accordingly, if we consider under the pressure Π and at the temperature $T + \delta T$ a univariant system in a state which is a state of equilibrium for the pressure Π and the temperature T, the system will undergo a change which, if it occurred under the pressure Π and at the equilibrium temperature T, would be accompanied by an increase in entropy, or, in other words, by an absorption of heat. Similarly, at a temperature slightly lower than the equilibrium temperature, the transformation is such that at the equilibrium temperature it would give out heat. This is Moutier's Theorem.[1]

Let us suppose finally that $\delta\Pi$ and δT are equal to the actual changes $d\Pi$ and dT of pressure and temperature as we pass from one point of the transformation curve to the next. Then the two states of equilibrium considered will pass into two adjacent states of equilibrium for which the potentials will again be equal. Accordingly we have

$$d\Phi_2 = d\Phi_1 ;$$

from which we obtain

$$V_2 d\Pi - H_2 dT = V_1 d\Pi - H_1 dT,$$

or finally

$$\frac{d\Pi}{dT} = \frac{H_2 - H_1}{V_2 - V_1} = \frac{Q}{T(V_2 - V_1)},$$

in which Q represents the heat absorbed by the system in passing from the state 1 to the state 2 at the temperature T and under the pressure Π. This is the well-known Clapeyron-Clausius formula.

Bordeaux, May 22, 1899.

[1] Moutier. Bulletin de la Société philomathique (3) 1, pp. 39 and 96 (1877). Duhem. Mécanique Chimique, Vol. I., p. 191.

HYDRATES IN SOLUTION

BY WILDER D. BANCROFT

On page 430 of the second edition of Nernst's '*Theoretische Chemie*' is to be found the following passage:[1] "We have hitherto excluded the possibility of the solvent taking part in the reaction and we will now determine how such a phenomenon is to be treated. The simplest case is that in which there is only one kind of molecule A in solution which reacts with the molecules of the solvent, water, for instance, in which case it forms a hydrate; we are then considering the reaction

$$A(H_2O)_n \rightleftarrows A + nH_2O,$$

which has the form of a dissociation equation. Let c be the concentration of the hydrated, c_1 that of the dehydrated molecules of the substance, A and c_2 the concentration of the water, then we have the equation

$$Kc = c_1 c_2^n.$$

Now it is to be noticed that c_2 is very large relatively to c and c_1, and therefore, especially when the solution is sufficiently dilute, the active mass of the solvent will change but slightly if the equilibrium is displaced in one direction or the other, i. e. *the active mass of the solvent is practically constant;* whence follows proportionality betweeen c and c_1, and in a dilute solution *the percentage of hydrated substance is therefore independent of the concentration*, a consequence of the mass law which has not hitherto received due attention."

This conclusion is of sufficient importance to call for a careful examination. The first objection to be made to it is that the tacit assumption has been made that no compounds of the form A_nH_2O can exist. It is a fact that most of the substances with

[1] Reprinted without change from page 219 of the first edition.

which we are familiar and which form hydrates do not crystallize with submultiples of water; but the water in the argument was merely selected so as to have a concrete case to discuss. If we assume the existence of a hydrate of alcohol, for instance, containing two or more of water, Nernst's reasoning shows that it would be decomposed by alcohol but not by water. This, however, is a hypothetical case which probably does not really interest anybody.

A more important question is whether Nernst's conclusions apply also to hydrated salts. A good many people are fairly certain that acetic anhydrid is hydrated when dissolved in water; they feel confident also that metaphosphoric acid takes up water when dissolved and they shrewdly suspect that something similar takes place with sulfur dioxid and trioxid. In view of these facts, they see no reason why sulfates, for instance, might not retain the so-called 'water of constitution' when in solution. Unfortunately, it is not clear from the text what Nernst thinks about the case of hydrated salts. He has omitted all reference to the possibility of electrolytic dissociation and yet a foot-note that he adds makes it improbable that he intends to exclude electrolytes. It will, however, be more profitable to consider what conclusions are permissible in regard to hydrates in solution rather than to speculate as to Nernst's meaning.

To simplify matters we will assume the validity of the mass law, the gas laws, and Ostwald's dilution law. We have then two reactions taking place simultaneously with changing concentration: a possible dehydration and a change in the electrolytic dissociation. Let A be the total amount of salt present at any moment, x the amount of anhydrous undissociated salt, y the amount of dissociated salt, and C the amount of water at any given dilution. The amount of hydrated salt will therefore be $A-x-y$ and we shall have two equations for equilibrium:

$$K\frac{x}{V}=\left(\frac{y}{V}\right)^{2} \tag{1}$$

$$K_1\frac{A-x-y}{V}=\frac{x}{V}\left(\frac{C}{V}\right)^{n} \tag{2}$$

Assuming with Nernst that C/V is a constant for dilute solutions we may write

$$K_2 \frac{A-x-y}{V} = \frac{x}{V} \qquad (3)$$

Combining (1) and (3) and writing K_3 for $K K_2$ we have

$$K_3 \frac{A-x-y}{V} = \left(\frac{y}{V}\right)^2 \qquad (4)$$

from which follows that the percentage hydration decreases with decreasing concentration or that hydrated salts are decomposed by water.

The question at once comes up as to the effect of the presence of hydrates in solution on the Ostwald dilution law as usually expressed. What we determine from the conductivity measurements is the percentage dissociation, and the Ostwald dilution law is therefore written:

$$K_4 \frac{A-y}{V} = \left(\frac{y}{V}\right)^2 \qquad (5)$$

which is not the same as equation (1) or equation (4). It is however true, in case these two equations hold, for subtracting equation (1) from (4) we have

$$\frac{KK_3}{K-K_3} \frac{A-y}{V} = \left(\frac{y}{V}\right)^2 \qquad (6)$$

which becomes identical with equation (5) provided we write

$$K_4 = \frac{KK_3}{K-K_3}.$$

We thus see that the existence of dissociating hydrates in solution would not suffice to account for the variations from Ostwald's dilution law and conversely that the fact that a binary electrolyte follows Ostwald's dilution law does not prove that the undissociated substance is not hydrated in solution.

In the discussion up to this point it has been assumed that there was equilibrium between the anhydrous solute and the dissociation products. This is not necessarily the case to any measurable extent, and the reaction may be considered as represented by the equation.

$$RX(H_2O)_n \rightleftharpoons \overset{+}{R} + \overset{-}{X} + nH_2O.$$

In this case, the hydrate will dissociate with increasing dilution and there is nothing in the fact of a hydrate being present in solution to prevent the dilution law from holding.

The anhydrous compound need not be an electrolyte, but may become one when hydrated, as in the case of sulfur trioxid. The general equation would then be

$$XHOH \rightleftarrows X + H_2O$$

$$XHOH \rightleftarrows \overset{+}{H} + \overset{-}{XHO}.$$

Here too there will be complete electrolytic dissociation at infinite dilution. Still another possibility is that one of the ions may be hydrated. We have a case of this with metaphosphoric and orthophosphoric acids

$$HPO_3H_2O \rightleftarrows HPO_3 + H_2O$$

$$HPO_3H_2O \rightleftarrows H + PO_3H_2O.$$

This is not an ideal case because metaphosphoric acid is an electrolyte, because practically no metaphosphoric acid remains in solution at equilibrium, and because orthophosphoric acid is a dibasic acid at great dilutions. If all these points could be eliminated we should get equations (1) and (2) over again, and the effect of dilution would be the decomposition of the hydrated compound though not of the hydrated ion.

We may therefore draw the following conclusions:

1. Hydrated electrolytes are decomposed by dilution.

2. The presence in solution of a hydrated electrolyte will not account for variations from Ostwald's dilution law except in so far as it is not permissible to treat the concentration of the water as constant.

3. Treating the concentration of the water as constant the ratio of the concentrations of a hydrated and a dehydrated ion will remain the same, provided there is no secondary electrolytic dissociation.

Cornell University

NEW BOOKS

A Short Manual of Analytical Chemistry. *By John Muter. Second American Edition. 16 × 25 cm; pp. xiii and 228. Philadelphia: P. Blakiston, Son and Co., 1898. Price: cloth $1.25.* — This book was originally written for the use of pharmaceutical students, and is described by the author as "a concise and consequently low-priced manual designed to introduce students to the chief developments of analytical chemistry."

In its scope the work is very different from any other of the same size with which the reviewer is familiar. After a short introduction on 'the processes employed by chemists' qualitative analysis is taken up, including that of the commoner metals, 57 acids and 86 'alkaloid and organic bases commonly employed in medicine.' Quantitative analysis comes next, occupying pages 94 to 166, of which 33 are devoted to volumetric and colorimetric analysis, 20 to gravimetric, and six to ultimate organic analysis. Besides this, the book contains three chapters on special processes for the analysis of (a) water, air, and food, (b) drugs, urine, and urinary calculus, and (c) gas, with polengation and spectrum analysis, etc., respectively.

By dint of large pages, thin paper, a concise style of writing, the introduction of tables, and the use of numerous varieties of type, the author has found it possible to condense all this matter into a book but little over half an inch thick. None of the 'Standard' methods seem to have been left out, perhaps the only exception being the omission of those volumetric processes commonly known as 'extensions' of the alkalimetric and acidimetric methods. It goes without saying that in so eminently 'practical' a recipe book a 'theoretical' part would seem strangely out of place, and has very properly been dispensed with.

Although the work can hardly be recommended to those entering upon the study of chemistry, as part of a general education, yet if there be a 'long-felt want' for a short account of *all* the important analytical methods in one compact volume, Muter's 'Manual' certainly fills it. *W. Lash Miller*

A Short Course in Inorganic Qualitative Analysis. *By J. S. C. Wells. First Edition. 13 × 19 cm; pp. vi and 294. New York: John Wiley & Sons, 1898. Price: cloth $1.50.* — "The separations are presented in the form of schemes accompanied by explanatory notes, and tables of scheme relations. . . . Chemical equations are freely used to explain the various reactions. . . . In the introduction a short explanation (ten pages) is given of these equations. . . . This, of course, belongs more properly to general chemistry, but experience has proved the average student to be wofully ignorant on this subject, and a brief exposition of the subject seemed necessary."

But although "the object in making all these tests and separations is to make [the student] familiar with certain chemical facts and their application",

and although "the first and most important point in any analysis is a thorough knowledge of the principle involved", no attempt is made to banish the student's "woful ignorance" of the simple generalizations that have been made concerning the behavior of salt solutions, with which he deals almost exclusively. The very conception of chemical reactions as in general reversible, to say nothing of the few simple causes which for the most part determine their direction, are nowhere discussed, — not even where (as in the formation of basic salts of Al and Bi, and in the reaction between HCl and Sb_2S_3) the reversibility of the reaction obtrudes itself in the most obvious way on the analyst's attention.

Although in the present state of elementary instruction in physics, and chemistry, it may not be advisable to introduce the beginner to electrochemical theories, the fundamental principle of reactions in salt solutions are too well founded and too easily grasped to be omitted altogether from any work that proposes to make the student "perfectly familiar with the conditions necessary for the successful performance of the operations in hand."

W. Lash Miller

A Laboratory Guide in Qualitative Chemical Analysis. *By H. L. Wells. First Edition. 15 × 23 cm; pp. vii and 189. New York: John Wiley and Sons, 1898. Price: cloth $1.50.* — The difficulties of teaching analytical chemistry in such a way as to prevent thoughtless and mechanical work on the part of the student are very well known; and every year sees the publication of at least half a dozen new treatises on the subject. The author of the present work, however, has adopted such radical methods as justify a much more extended notice of his 'Laboratory Guide' than is at all customary.

"The general plan . . . consists in giving directions for analysis without mentioning the results, and in requiring the student to determine for himself the result of the operations. . . . The student almost invariably performs his preliminary experiments with great care. . . . This is especially the case if the student understands that in the analysis of unknown mixtures, he will not be allowed to use any table or any abbreviated schemes of analysis. The notebook . . . should never be used in place of memory. At the outset, it should be understood that the student is required to remember the fact encountered."

The author's method of carrying out this 'general plan' may be gained from the following abridgment of a part of "*Chapter II, Group A* (*Fresenius's Group V, Div. I.*), *Radicals whose chlorids are insoluble or nearly insoluble in acidified solutions*" (directions as to methods of manipulations, etc., have been omitted).

"1. Find by experiment which of the 27 solutions (of salts provided by the laboratory) give precipitates when a few drops of hydrochloric acid, HCl, are added to 1 or 2 cc in a test-tube. Write the equations of the reactions and remember the fact observed in this experiment as well as in those which follow. Why are no precipitates produced in the solutions containing chlorides?

"2. Take . . . about 5 cc of each solution in which hydrochloric acid produces a precipitate, dilute it to ten volumes with distilled water . . . and add hydrochloric acid to a small portion as before. . . . Dilute some of the last solution ten times the same way. Calculating from the original strength of the solution, how much solid salt is present? Then go on, testing and diluting in the same manner, until the reaction disappears. From this experiment decide . . . whether or not the precipitation by hydrochloric acid is practically complete.

"3. To learn the process of analysis, take separately in small beakers 5 or 10 cc of the three solutions which give precipitates with hydrochloric acid, and in another beaker make a mixture of about the same quantities of these solutions. . . . To each solution . . . add hydrochloric acid . . . until no further precipitate is evident. . . . Filter into clean beakers, and add a little hydrochloric acid to the filtrate to make sure that enough has been used. The filtrate may be thrown away. . . .

"Treat the chlorid in the four filters with boiling water, and in each case catch the liquid which runs through, in a test-tube. To the liquid from the mixed chlorid, add a considerable quantity of dilute sulfuric acid, H_2SO_4. Find which of the metals has given the reaction by adding sulfuric acid in the same way to the liquids from the separated chlorid. Add sulfuric acid to a portion of the original solution of the nitrate of this metal, allow some of the precipitate to settle, pour off the liquid, and see if the precipitate dissolves in hot water like the chlorid.

"Continue the application of hot water . . . until sulfuric acid fails to give any precipitate in the washings, then upon all the filters pour ammonium hydroxide, NH_4OH. . . . Notice any change of color taking place, and from the single chlorid decide which metal it is which gives the reaction.

"Acidify the ammoniacal solution in the test-tubes with nitric acid, and decide which metal it is which gives the reaction. By experiment find if nitric acid gives a precipitate in solution of the nitrate of this metal. Can the precipitate be the nitrate of the metal? Analyze unknown solutions of this group. At least three correct analyses should be made."

"*Part II., Theory*" pp. 71–87 also differ markedly from the usual perfunctory paragraphs on the atomic theory, and on "writing equations" — containing as it does short chapters on 'chemical radical and formula', 'ionization and ions', 'precipitation', etc.; and indicating the consequences of the identity of solutions of 'reciprocal pairs of salts', the theory of the use of sodium acetate as a reagent, the simplification in inorganic analysis produced by the "circumstance that ionization takes place," etc., etc. Of necessity the space devoted to theory is limited, but there is at least an attempt to introduce modern conceptions into the analytical laboratory.

In "Part III., Descriptive Part," the various "inorganic radicals" are arranged in alphabetical order, and a word or two said about each. The reviewer hopes that in a subsequent edition, this part of the work will be considerably extended. As a whole page is devoted to each "radical" the change need involve no increase in the size of the book. On "lead," for example, there is a paragraph or two on the chlorid, sulfate, sulfid, and nitrate, but nothing at all is said about the chromate, basic chromate, or iodid, although these are among the most characteristic compounds of the metal and are consequently almost invariably employed as "confirmatory tests". *W. Lash Miller*

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry

General

A physical principle of development. *O. Wiedeburg. Wied. Ann.* **63,** *154* (*1898*). — No theory can give a full account of solids if it ignores hysteresis phenomena, and it is probable that something of the same sort may be true with regard to liquids and gases, though this cannot be affirmed positively. The author reiterates the importance of the views expounded in his first paper on irreversible processes (**1,** 693). *W. D. B.*

On irreversible processes, II, III. *O. Wiedeburg. Wied. Ann.* **62,** *652* (*1897*); **64,** *519* (*1898*). — The first paper of this series has already been reviewed (**1,** 693). The second paper deals with the laws of the resistance values; the third paper with the position of heat with respect to the other forms of energy. *W. D. B.*

The absolute temperature. *K. Schreber. Wied. Ann.* **64,** *138*; **65,** *648* (*1898*). — The author adopts Lord Kelvin's original definition. The difference of the temperatures of two substances, between which a reversible cycle takes place such that the heat energy Q_1 is taken from the hotter substance and the heat energy Q_2 is given off to the colder substance, is given by the equation

$$t_1 - t_2 = \frac{1}{\log^2} \cdot \log \frac{Q_1}{Q_2} .$$

This the author calls the absolute temperature scale because it is independent of any actual substance. One degree on this scale corresponds roughly to 221.8° on the hydrogen scale, so that it would be necessary to select some smaller unit than the absolute unit. The author then discusses this scale at length. *W. D. B.*

Remarks on the absolute temperature. *F. Auerbach. Wied. Ann.* **64,** *754* (*1898*). — The objection is made to Schreber's absolute temperature scale (preceding review) that it has no zero point. Instead of this geometrical absolute temperature scale, the author prefers an arithmetical absolute temperature scale which starts from −273°. *W. D. B.*

The question of the absolute temperature. *O. Wiedeburg. Wied. Ann.* **65,** *921* (*1898*). — The point is taken that what temperature scale is defined as the 'absolute' scale depends on the definition of 'quality of heat'. *W. D. B.*

On the measurement of flame temperature by a thermocouple. *F. Berkenbush. Wied. Ann.* **67,** *649 (1899).* — The work is undertaken to test the methods of Nernst for measuring flame temperatures. Two such methods have been given, the first depends on extensive extrapolation from considerations of the rate of heating and cooling the couple at different temperatures and does not give good results. The second method consists in electrically heating the thermocouple in the flame itself. A study of the loss of heat from the couple electrically heated without the flame gives the necessary data for arriving at considerations of the heat loss from the couple, and hence getting at the true temperature of the flame. The most interesting and valuable part of the paper is the author's work on the rate of loss of heat in different vacuo. From thermochemical data the temperature of the Bunsen flame should be according to the author 1820°. From his calculations with the thermocouple he makes the maximum temperature 1830°. Previous results differ somewhat, the closest to the author's being that of Waggener, 1785°. *H. T. B.*

On energetics. *P. Gruner. Zeit. phys. Chem.* **23,** *636 (1897).* — An attempt to show mechanics may be based on energetics. *W. D. B.*

Graphics of the thermodynamic function. *W. Fox. Jour. Franklin Inst.,* **145,** *214 (1898).* — An article showing that "graphics can be applied even to the mystical function Φ and to all theorems depending on it." *W. D. B.*

One-Component Systems

On the separation of helium from a natural compound with marked evolution of heat and light. *J. Thompson. Zeit. phys. Chem.* **25,** *112 (1898).* — Twenty years ago the author noticed that when a form of yttrocerite from Sorgtut was heated in a platinum vessel the powder suddenly became incandescent; but that this phenomenon could not be made to occur a second time. The cause of this could not be ascertained at that time; but it has now been found that the intense heat was due to the evolution of helium. *W. D. B.*

The homogeneity of helium. *W. Ramsay and M. W. Travers. Zeit. phys. Chem.* **28,** *135 (1898).* — It was found by Ramsay and Collie (**1,** 310) and by Hagenbach (**1,** 381) that helium could apparently be separated by diffusion into a heavier and a lighter gas. This point has been taken up again and the authors have made an enormous number of diffusion experiments, the final result of which is that the whole trouble was caused by the presence of one per cent or less of argon. Reasons are given for supposing that another element (next review) will be discovered. *W. D. B.*

On a new constituent of atmospheric air. *W. Ramsay and M. W. Travers. Zeit. phys. Chem.* **26,** *362 (1898).* — In the residue left after a partial fractional distillation of liquid air, the authors have found a new gas showing a spectrum line very close to D and a green line 5568.8 fully as bright as the green line of helium. The new gas is monatomic; the present density is 22.51, oxygen being sixteen. It is believed, however, that the new element, to which the name krypton, Kr, is given, may prove to have a density of 40 and an atomic weight of 80. *W. D. B.*

The permanent modifications of glass and the displacement of the zero in thermometers. *L. Marchis. Mém. Soc. Sci. Bordeaux* (*5*) **4**, *1*; *Jour. de Phys.* (*3*) **7**, *573* (*1898*); *Zeit. phys. Chem.* **29**, *1* (*1899*). — Reviewed (**3**, 109) from the author's thesis. The first paper is the thesis in full; the second is a brief restatement of the first four chapters; the third is a condensed form of the thesis.

Extension of the law of Boyle, van der Waals, Gay Lussac to homogenous liquids. The kinetics of liquids. Extension of the law of Avogadro to homogeneous liquids. *J. Traube. Wied. Ann.* **61**, *380*, *391*, *396* (*1897*). — See the paper by Nasini (**2**, 59).

On the behavior of iron with reference to the law of Wiedemann and Franz. *F. A. Schulze. Wied. Ann.* **63**, *23* (*1897*). — Wiedemann and Franz found that the ratio of the heat conductivity to the electrical conductivity had nearly the same value for all metals. This is distinctly not the case with different samples of iron and steel. *W. D. B.*

On the latent heat of vaporization. *J. A. Groshans. Wied. Ann.* **64**, *778* (*1898*). — It is pointed out that if we assume Trouton's law and that the gas law holds for saturated vapors, it follows that one small calorie will vaporize equal volumes of vapor from any liquid at 76 cm and the boiling-point, this volume being 3.87 cc. There is also a discussion of the two classes into which Trouton's law divides all liquids, that for which the constant is 21.139 and that for which it is 25.89 and the bearing of these two constants on the law of corresponding temperatures. *W. D. B.*

On expansion, also with reference to the latent heat of vaporization. *J. A. Groshans. Wied. Ann.* **64**, *789* (*1898*). — The author expresses the ratio of the volumes of saturated vapor and of liquid in terms of his 'variable constant x, (**1**, 741). *W. D. B.*

Contributions to the kinetic theory of polyatomic gases. *H. Staigmüller. Wied. Ann.* **65**, *655* (*1898*). — The diatomic gases are divided into two classes in one of which the distance between the two atoms remains constant, while in the other, it is subject to periodical changes. Grant this and all goes well. *W. D. B.*

Attempt at a theoretical deduction of the constants of the law of Dulong and Petit. *H. Staigmüller. Wied. Ann.* **65**, *670* (*1898*). — The deduction rests on the postulate that in gases the temperature is a function of the kinetic energy of the forward movement of the molecules, while in solids it is a function of the kinetic energy of an atom vibrating about a definite point of equilibrium. *W. D. B.*

Significance of the constant HV/T. *E. Boggio-Lera. Nuovo Cimento.* (*4*) **5**, *293* (*1897*). — In the expression HV/T, H is the pressure in dynes per square centimeter of one gram of hydrogen, V the volume in cubic centimeters, and T the absolute temperature. The author claims that this expression is the mechanical equivalent of one calorie. *W. D. B.*

On the note of Boggio-Lera as to the significance of the constant HV/T. *C. del Lungo. Nuovo Cimento,* (*4*) **6,** *55, 273* (*1897*). — Two criticisms of Boggio-Lera's hypothesis (preceding review). *W. D. B.*

On the constant HV/T. *P. Joubin. Nuovo Cimento,* (*4*) **6,** *53* (*1897*). — A criticism of Boggio-Lera's hypothesis (two reviews back). *W. D. B.*

Reply to the criticisms of my note on the constant HV/T. *E. Boggio-Lera. Nuovo Cimento,* (*4*) **6,** *210, 331* (*1897*). — Two rejoinders to the criticisms of his hypothesis (preceding two reviews). *W. D. B.*

The law of corresponding states and the characteristic equation of liquids. *C. Raveau. Jour. de Phys.* (*3*) **6,** *432* (*1897*). — The author has made use of a modification of Amagat's method (**1**, 66), and uses logarithmic coordinates in plotting his curves. *W. D. B.*

Theory of liquids with simple molecules. *J. Bakker. Jour. de Phys.* (*3*) **6,** *577* (*1897*). — Reviewed (**1**, 377) from the more extended article, Zeit. phys. Chem. **21,** 497 (1896).

Densities, molecular volumes, compressibility and dilatation of gases at different temperatures and ordinary pressures. *A. Leduc. Jour. de Phys.* (*3*) **7,** *5, 189* (*1898*). — Reviewed (**1**, 510; **3**, 114, 115) from the brief notes, Comptes rendus **124,** 285; **125,** 297, 397, 571, 703, 768 (1897).

Relation among the characteristic laws of perfect gases. *G. Bakker. Jour. de Phys.* (*3*) **7,** *152* (*1898*). — See **1**, 198, 688.

On the thermal properties of saturated fluids. *E. Matthias. Jour. de Phys.* (*3*) **7,** *397* (*1898*). — The author discusses the adiabatic expansion of saturated vapors, the specific heat at constant volume of saturated vapors, and other similar matters. *W. D. B.*

Experiments on the influence of pressure on the melting-point. *R. Demerliac. Jour. de Phys.* (*3*) **7,** *591* (*1898*). — Substantially a repetition of a former paper (**1**, 505).

The specific heat of anhydrous liquid ammonia. *L. A. Elleau and W. D. Ennis. Jour. Franklin Inst.* **145,** *189, 280* (*1898*). — The specific heat of liquid ammonia was found to be 1.02 at 0°. *W. D. B.*

On the melting-points of organic substances. *A. P. N. Franchimont. Rec. Trav. Pays-Bas,* **16,** *126* (*1897*). — Reviewed (**1**, 682) From Kon. Akad. Wetensch, Verslag. Amsterdam, **1896,** 156.

Two-Component Systems

On heats of solution and dilution. *E. v. Stackelberg. Zeit. phys. Chem.* **26,** *533* (*1898*). — The author has determined the thermochemical heats of solution and the heats of dilution for the nitrate, chlorate, bromate, iodate, perchlorate, bichromate, and chlorid of potassium; for sodium chlorid, sodium

nitrate, ammonium chlorid, barium nitrate, and cane sugar. The curves for the change of the heat effects with the concentration vary very much with the temperature, even intersecting in some cases. There are appended discussions of the temperature coefficients; of the relation between heat of dilution and internal pressure; of the relation between heat of solution, and solubility. It is also pointed out that from the course of the vapor-pressure curves, so far as known, the solubility curve for sodium sulfate with ten of water would probably, if it could be realized, cut the solubility curve for sodium sulfate with seven of water at some temperature below zero, in which case it would follow that the heat of hydration from $Na_2SO_4 7H_2O$ to $Na_2SO_4 10H_2O$ would take place without heat effect at some temperature. *W. D. B.*

Perborates and their constitution. *S. Tanatar. Zeit. phys. Chem.* **26,** *132 (1898).* — Sodium perborate can be made by electrolyzing a concentrated solution of sodium orthoborate or by oxidizing the same solution with hydrogen peroxid. Ammonium perborate can be made in the same way, but must be precipitated with alcohol. The heats of solution and of decomposition were determined. *W. D. B.*

The reliability of the dissociation-values determined by electrical conductivity measurements. *A. A. Noyes. Jour. Am. Chem. Soc.* **20,** *517;* **26,** *699 (1898).* — The author considers van Laar's correction of the heat of solution formula (**3,** 66) erroneous, because his two equations lead to different results for complete dissociation, and because there is no term for the change of dissociation with the temperature. It is further claimed that the thermodynamical heat of solution is "the heat which is absorbed by the dissolving of one molecule of the substance in a solution of *unchangeable* concentration; namely, that corresponding to the equilibrium", whereas van Laar assumes differential changes of concentration. The author then gives a deduction of van 't Hoff's formula and discusses some of the other points raised by van Laar. *W. D. B.*

Reply to the objections of A. A. Noyes to my solubility formula. *J. J. van Laar. Zeit. phys. Chem.* **27,** *337, (1898).* — It is claimed that all the points raised by Noyes (preceding review) are wrong; that Noyes's deduction of the van't Hoff formula is wrong and that Noyes's own line of reasoning really leads to the van Laar formula. *W. D. B.*

The thermodynamical expressions for the heats of solution and of dissociation for electrolytes. *A. A. Noyes. Zeit. phys. Chem.* **28,** *431 (1898).* — A particularized disclaimer of the points made by van Laar (preceding review), together with the statement that van Laar has used the 'theoretical' heat of solution instead of the 'integral' heat of solution. *W. D. B.*

The heat of solution. Last word in reply to Mr. Noyes. *J. J. van Laar. Zeit. phys. Chem.* **20,** *159 (1899).* — In this article we really get somewhere. Van Laar admits that he uses the 'theoretical' heat of solution in his calculations, as claimed by Noyes (preceding review); but exults in the fact that that is what he should use and says that the whole trouble has come from the use of the wrong heat of dilution by Noyes. The counter-rejoinder has not yet had time to appear, but may reasonably be expected.

This series of articles is an admirable instance of how not to do things. There will always be irreconcilable differences of opinion, and it is desirable to hear both sides; but that is no reason why the whole debate should be published. In the present instance, it would have been much better if Messrs. Noyes and van Laar had corresponded privately until they had agreed as to the points on which they differed, and had each published a brief for his side which had been submitted to and approved by the other man. It is of some importance whether van Laar or Noyes be right. It is of absolutely no importance whether Noyes misunderstood van Laar in certain points or van Laar misunderstood Noyes. Special stress has been laid on this matter because there seems to be a general opinion that a public polemic is desirable. In two instances in which the reviewer has taken occasion to write privately, calling attention to what seemed to him an inaccuracy, he has received the answer: "If you will publish your comments, I shall be happy to discuss them in the scientific journals." Few things could be more unfortunate than this state of mind.

W. D. B.

Researches on the compressibility of solutions. *H. Gilbault. Zeit. phys. Chem.* **24,** *385* (*1898*). — Reviewed (**1,** 602) from Ann. Fac. Sci. Toulouse, **11,** 131 (1897).

Mr. Abegg's criticism of freezing-point determinations. *C. Dieterici. Wied. Ann.* **64,** *809* (*1898*). — The point is made that the author's conclusions (**2,** 262) referred expressly to concentrations between normal and tenth-normal; Abegg's assumption (**2,** 399) of an extrapolation to very dilute solutions is unjustified. *W. D. B.*

On the melting-point of the alloy of aluminum and antimony corresponding to the formula AlSb. *E. van Aubel. Jour. de Phys.* (*3*) **7,** *223* (*1898*). — The compound AlSb melts at 1070°–1080°. *W. D. B.*

On the constitution of eutectic alloys. *J. Charpy. Jour. de Phys.* (*3*) **7,** *145* (*1898*). — Reviewed (**2,** 401) from Séances. Soc. Phys. Paris, **1897,** 87.

Poly-Component Systems

Absorption of liquids by textile stuffs. *L. Vignon. Bull. Soc. Chim. Paris,* (*3*) **19,** *919* (*1898*) — Reviewed (**3,** 415) from Comptes rendus, **127,** 73 (1898).

On the limits of inflammability of gaseous mixtures. *H. Le Chatelier and O. Boudouard. Bull. Soc. Chim.* (*3*) **19,** *483* (*1898*). — Reviewed (**3,** 427) from Comptes rendus, **126,** 1344, 1510 (1898).

Molecular weights in solutions of permanganates, perchlorates, and periodates. *J. M. Crofts. Jour. Chem. Soc.* **73,** *593* (*1898*). — The author used hydrated sodium sulfate as solvent and obtained values pointing to the formulas $KMnO_4$, $KClO_4$ and KIO_4. This confirms the results obtained by others.

W. D. B.

Complete calorimetric study of a salt. *E. Monnet. Mém. Soc. Sci. Bordeaux*, **3**, *41* (*1898*). — This is indeed a complete calorimetric study of sodium acetate and water; the paper may be taken as a model. *W. D. B.*

On the dissociation of selenium hydrid. *H. Pélabon. Mém. Soc. Sci. Bordeaux*, **3**, *141* (*1898*). — The author's thesis; reviewed (**3**, 178) from Zeit. phys. Chem. **26**, 659 (1898).

On the solubility of mix-crystals and the size of the crystal molecule. *A. Fock. Zeit. Krystallographie*, **28**, *337* (*1897*) — A study of the solubility of fifteen pairs of salt with which solid solutions are impossible. The distribution law did not apply as the author thought it should, and modifications were suggested which were afterwards dropped. [See next review]. *W. D. B.*

On dissociation in mixed salt solutions. *A. Fock. Zeit. phys. Chem.* **25**, *74* (*1898*). — In a previous paper (preceding review) it had been found that the distribution law did not apply to the form $c(1-\gamma)/x$, where c is the concentration and γ the degree of dissociation in the liquid phase, and x the concentration in the solid phase. On the other, it was found that $c(1-\gamma)/x + c^2\gamma^2/x =$ const. The object of this paper is to show that if there is an error in the determination of γ the formulas $c(1-\gamma)/x =$ const., and $c^2\gamma^2/x =$ const. might appear to be wrong and yet the sum of the left-hand terms might yet be constant owing to the errors cancelling. The results of the first paper, therefore, do not contradict the distribution law and the author's conclusion holds that in the crystals the molecular weight equals the formula weight. *W. D. B.*

Equilibria in three-component systems in which two liquid phases can occur. III. *F. A. H. Schreinemakers. Zeit. phys. Chem.* **25**, *305* (*1898*); *Arch. Néerl.* (*2*) **2**, *144* (*1899*). — The discussion is extended to cover the cases in which two of the components may be present simultaneously. After a general treatment of the equilibrium phenomena, the author considers the change of temperature necessary to keep solid A in equilibrium with two liquid phases at constant pressure when a third component C is added. He distinguishes the two cases in which C is more or is less soluble in the liquid phase in which A is present in excess. He then points out that the temperature will fall in the first case and rise in the second. [This is not necessarily true, unless the ratios of A to B in the two phases diverge on the addition of C. For instance, adding acetic acid to a mixture of benzene and water lowers the temperature at which solid benzene appears in spite of the fact that more acetic acid goes into the water than into the benzene.] Instances are given to support this view together with a thermodynamical proof of the theorem. *W. D. B.*

Generalization of the considerations in the preceding paper on the influence of foreign substances on the inversion temperature. *H. A. Lorentz. Zeit. phys. Chem.* **25**, *332* (*1898*); *Arch. Néerl.* (*2*) **2**, *174* (*1899*) — For the displacement of the inversion temperature for a solid, and two liquid phases at constant pressure on the addition of a third component C, the author deduces the formula

$$\theta = \frac{T o^2}{W} k_c R_c (c - c'),$$

in which θ is the change of temperature, To the inversion temperature when no C is present, W the heat of solution, k, the molecular weight of C (assumed to be the same in the two phases), R, the gas constant for C, c and c' the concentrations in the liquid phases. This formula is practically identical with one given by Schreinemakers (preceding review). *W. D. B.*

Equilibria in the system: water, ether, and ethylene cyanid. *F. A. H. Schreinemakers. Zeit. phys. Chem.* **25,** *543 (1898).* — The data for the two-component systems, water and ethylene cyanid, water and ether, have already been determined (**2,** 264, 265). In the system, ether and ethylene cyanid, there is a quadruple point at about 33° with two liquid phases and vapor in equilibrium with solid ethylene cyanid. The temperature of this point may be higher because traces of moisture lower it very much. In the three-component system there is a quintuple point at −45° with ice and solid ethylene cyanid in equilibrium with two liquid phases and vapor. Between + 1° and + 2°, there is another quintuple point with solid ethylene cyanid in equilibrium with three liquid phases and vapor. Some of the boundary curves have been followed a short way and an exhaustive discussion of the system is given. *W. D. B.*

Equilibria in the system: water, benzoic acid and ethylene cyanid. *F. A. H. Schreinemakers. Zeit. phys. Chem.* **26,** *237 (1898).* — This system was selected as being a case in which two liquid phases occur with two pairs of components, but not with the other pair. At 11.5° there is a quintuple point with benzoic acid and ethylene cyanid in equilibrium with two liquid phases and vapor. The two liquid phases become identical at 51°, the phases then being benzoic acid, solution and vapor. Starting from the system, benzoic acid and water, and adding ethylene cyanid, we find that benzoic acid can exist in equilibrium with two solutions and vapor from 95° down to 87°, at which latter temperature the two liquid phases become identical. A discussion of the isotherms completes the paper. *W. D. B.*

Equilibria in the system: water, alcohol and ethylene cyanid. *F. A. H. Schreinemakers. Zeit. phys. Chem.* **27,** *95 (1898).* — This system differs from the one with water, benzoic acid and ethylene cyanid as components in that there is no consolute temperature when a solid phase is present. The boundary curves for solid, two solutions and vapor obtained by adding alcohol to water and ethylene cyanid, meet the corresponding curves obtained by adding water to alcohol and ethylene cyanid. Many points on the boundary curves and on the isotherms have been determined. *W. D. B.*

Aqueous solutions of two salts with a common ion. II. *C. Hoitsema. Zeit. phys. Chem.* **28,** *312 (1898).* — The author has determined the solubility at 20.1° of mixtures of sodium salicylate and salicylic acid, and of potassium hippurate and hippuric acid. In both cases a double salt is formed; in both cases adding the salt causes the solubility of the acid to decrease, pass through a minimum and then increase; and in both cases addition of the acid causes little or no change in the solubility of the salt. The form of the isotherm in each case is that predicted by the author in his first paper (**2,** 402). *W. D. B.*

On the conductivity method of studying moderately dilute aqueous solutions of double salts. *F. G. MacGregor and E. H. Dalhousie. Phil. Mag.* [5] **46,** *509* (*1899*). — The following conclusions are drawn :

1. In all cases investigated so far, the conductivity of solutions containing two electrolytes with a common ion is calculable by means of the dissociation theory up to a concentration of about one gram equivalent per liter.

2. The conductivity of solutions of the double sulfate of copper and potassium is similarly calculable only up to a concentration of about 0.1, and has at concentration 1 a considerably smaller value than that calculated on the assumption that no double molecules are present.

3. The solutions of double salt have at concentration unity an appreciably smaller conductivity than the equivalent mixtures.

4. The conductivities of mixtures of equimolecular simple solutions of zinc and copper sulfates and of potassium and sodium sulfates are calculable within the limits of observational error up to a concentration unity; and therefore the non-calculability in the case of the double salt solutions is probably not due to defective data.

5. The differences between the observed and calculated values of the conductivity of the double salt solutions and of the equivalent mixtures, and between the observed values in these two sets of solutions, are such as could be accounted for by the presence of double molecules in both, and their presence in slightly greater numbers in the double salt solutions than in the equivalent mixtures. *W. D. B.*

On the mixed halid salts of lead. *V. Thomas. Bull. Soc. Chim. Paris,* (*3*) **19,** *598* (*1898*). — Reviewed (**3,** 420) from Comptes rendus, **126,** 1349 (1898). *W. D. B.*

Equilibrium in systems of three components where two liquid phases may appear. I., II. *F. A. H. Schreinemakers. Arch. Néerl.* (*2*) **1,** *411 ;* **2,** *21* (*1898*). — Reviewed (**1,** 597 ; **2,** 62, 264) from Zeit. phys. Chem. **22,** 93, 515 ; **23,** 417, 649 (1898).

Fergusonite, an endothermal mineral. *W. Ramsay and M. W. Travers. Zeit. phys. Chem.* **25,** *568* (*1898*). — Fergusonite is a black, brilliant, homogeneous mineral, like obsidian in appearance, but very much denser. It consists chiefly of the oxids of niobium, tantalum, yttrium, erbium, and cerium. When heated to about 500° it gives off helium with marked evolution of heat and becomes less dense. The heat evolved was measured and found to be 8.09K per gram of mineral. *W. D. B.*

Osmotic pressure and cryoscopy. *A. Reychler. Bull. Soc. Chim.* (*3*) **19,** *102* (*1898*). — A reply to the theoretical considerations of Crompton (**2,** 140). *W. D. B.*

Velocities

On the determination of diffusion coefficients by the electrolytic method of H. F. Weber. *W. Seitz. Wied. Ann.* **64,** *759* (*1898*). — The author found many difficulties in applying Weber's method, chief among these being the impossi

bility of keeping the two electrodes identical electrically. There was always a difference, due either to irregularities or to occlusion. To get round this, he subtracted a constant value from all the readings in any one series. This correction was calculated by means of an imposing formula; but the value taken was really the one which would make the diffusion coefficient most nearly constant. Experiments were made with zinc sulfate, acetate and formate; with cadmium sulfate, lead acetate and silver nitrate. In the only case, zinc sulfate, where comparisons could be made with data obtained by other methods, the author's values were low; but he attributes this to the fact that he took especial precautions to keep the solutions from being jarred. *W. D. B.*

Rate of escape of ammonia from aqueous solutions. *E. P. Perman. Jour. Chem. Soc.* **73,** *511 (1898).* — A large number of experiments have been made on the rate at which ammonia escapes from a solution when dry air is bubbled through it. It was found that the results could be expressed very satisfactorily by the equation $\log q = a - bV$, where q is the amount of ammonia in solution at any time, V is the volume of air passed through, and a and b are constants. When the air is drawn through at a constant rate, the equation may be written $\log q = a - b't$, where t is the time. Since a is evidently the logarithm of the concentration at the beginning of the experiment, we may throw the equation into a more familiar form by making $a = \log A$, $q = A - x$, and $b = k$, when we have

$$\log \frac{A}{A-x} = kt.$$

If we assume that the air is saturated, the amount of ammonia carried off in each instant will be proportional to the partial pressure of the ammonia vapors. Perman's results are exactly what should take place in case ammonia followed Henry's law. More accurately worded, ammonia follows Henry's law within the limit of error of Perman's experiments. *W. D. B.*

On the velocity of reversible reactions. *P. T. Muller. Bull. Soc. Chim. Paris, (3)* **19,** *337 (1898).* — It is stated, but not proved, that the reaction velocity equations for reversible reactions of the first and second order may be replaced by equations for irreversible reactions of the same order. (See **3,** 41). *W. D. B.*

Electromotive Forces

Physical chemical studies on the Weston normal cell. *P. Kohnstamm and E. Cohen. Wied. Ann.* **64,** *344 (1898).* — At 15° there is an inversion point at which one modification of $3CdSO_4.8H_2O$ is in equilibrium with another modification of the same salt. This was shown by solubility determinations, by experiments with an inversion cell and by measurements with the dilatometer. The Weston cell should therefore not be used at temperatures below 16°; on the other hand, it can be used at all temperatures above this up to 70° where the next inversion point occurs. *W. D. B.*

On the behavior of so-called unpolarized electrodes to the alternating current. *E. Warburg. Wied. Ann.* **67,** *493 (1899).* — As a preparation for the paper by Neumann the author reprints and to a certain extent reconsiders his

theory, published in 1896, for the effect of alternating currents on unpolarized electrodes. *H. T. B.*

On the polarization capacity of reversible electrodes. *Elsa Neumann. Wied. Ann.* **67**, *500* (*1899*). — The application of experimental data to the verification of Warburg's theory is the gist of the present paper. The author reiterates to a large extent the theory of the method. It can only be applied to the case of a mixture of two electrolytes with a common anion, and the cases given are those of mercury electrodes in a sulphuric acid solution of mercuric sulphate and silver electrodes in a nitric acid solution of silver nitrate. In the former very fair agreement is obtained but in the latter trouble was experienced owing to the too rapid change in capacity. The author points out the impossibility of applying the theory with the present measuring instruments, to the case of a single electrolyte. Considerable space is devoted to a discussion of the case when the current density may not be neglected in the general expression. An experimental verification with the mercury cell with varying current densities agrees very fairly well with what the theory should allow. A somewhat long discussion of the methods for estimating polarization capacity is included in the paper. In conclusion the author states that the ratification of the theory depends :

1. On the dependence of the capacity on the alternations.
2. On the dependence of the resistance change on the alternations.
3. On the absolute size of the phase displacement.
4. On the dependence of the capacity on the concentration of the metal salt.
5. On the dependence of the capacity on the current density.
6. On the absolute value of the capacity. *H. T. B.*

On photoelectric currents. *G. C. Schmidt. Wied. Ann.* **67**, *563* (*1899*). — A study of the action of light on pure metal surfaces in solutions of a salt of the same metal shows that there is no photoelectric reaction. The author considers any effect that has already been noted to be due to the action of the light in diminishing polarization, or some effect on the gas occluded on the metal surface. A study of copper oxid electrodes, however, yields some interesting results. A study is first made of cuprous and cupric oxid electrodes in potassium hydrate solution in order to find out in just what way the E.M.F. set up changes with time. First one electrode is illuminated, and then the other to study their photoelectric properties. A considerable change takes place between the electrodes in solution after first setting up, during which the E.M.F. sinks. Light has no action on the cuprous oxid electrode, but on the cupric oxid electrode after the E.M.F. has reached its lowest limit it has a positive effect. Red light has a positive effect on an electrode of high E.M.F., while violet light has a negative effect on the same electrode. In the first case the author considers the light causes an increase in the solution tension of the oxygen, and in the second the light causes a quicker change from the modification of high potential to that of lower. *H. T. B.*

Theory of the Hall effect in a binary electrolyte. *F. G. Donnan. Phil. Mag.* [*5*] **46**, *405* (*1898*). — The author deduces the formula

$$\frac{de}{dz} \Big/ \frac{d\pi}{dx} = \frac{1}{2}(U - V)H.$$

Where de/dz is the potential gradient of Hall effect, $d\pi/dx$ the potential gradient of the primary current, H the magnetic field-strength, U and V the velocities acquired under unit potential gradient by a gram-molecule of positive and negative ionic matter respectively. This formula is then applied to some data for copper sulfate furnished by Bagard. The calculated value is about 16×10^{-13}, while Bagard claimed to have found 0.39×10^{-5}. The author concludes that "Bagard has measured a phenomenon not contemplated in the foregoing theory." *W. D. B.*

On standard high resistances. *F. B. Fawcett. Phil. Mag.* [5] **46,** *500* (*1898*). — Excellent high resistances are obtained by depositing platinum, gold, or a mixture of the two on a glass strip by dispersion from a metallic cathode, heating in oil, and making a series of alternating scratches until the resistance has been increased to the desired value. *W. D. B.*

The Jacques carbon battery. *J. W. Langley. Jour. Franklin Inst.*, **146,** *224* (*1898*). — The result of the experiments is that the action in the cell is thermoelectric in nature. This explanation will hardly be accepted by any one who has read the paper by Liebenow and Strasser (**1,** 616). *W. D. B.*

Electrolysis and Electrolytic Dissociation

On the conductivity of electrolytes in organic solvents. *P. Dutoit and L. Friderich. Bull. Soc. Chim. Paris,* (*3*) **19,** *321* (*1891*). — From conductivity measurements with eighteen solvents the authors conclude "that the values of μ_∞ for the same electrolyte in different solvents varies directly with the degree of polymerization and inversely as the coefficient of viscosity." [For a discussion of this paper see **3,** 12.] *W. D. B.*

Contribution to the study of the electrical conductivity of salt solutions. *R. Goldschmidt and A. Reychler. Bull. Soc. Chim. Paris,* (*3*) **19,** *675* (*1898*). — In order to use smaller quantities of solution than in the Kohlrausch method, the authors have a movable electrode adjustable by a micrometer. They find that their results tend to be too high, presumably owing to a change of the lines of force. *W. D. B.*

On the production of crystallized tungsten by electrolysis. *L. A. Hallopeau. Bull. Soc. Chim. Paris,* (*3*) **19,** *997* (*1898*). — Reviewed (**3,** 429) from Comptes rendus, **127,** 755 (1898).

Dielectricity and Optics

On certain emission spectra of cadmium and zinc, and of the halid compounds of mercury and certain other metals. *A. C. Jones. Wied. Ann.* **62,** *30* (*1897*). — Reviewed (**1,** 628) from the author's inaugural dissertation.

On a new kind of rays. *W. C. Röntgen. Wied. Ann.* **64,** *1, 12, 18* (*1898*). — Reprinted from the Sitzungsber. Würzburger, Physik. Med. Gesellschaft, and the Sitzungsber. Akad. Wiss. Berlin.

On the colored alkaline halids. *E. Wiedemann and G. C. Schmidt. Wied. Ann.* **64,** *78* (*1898*). — The authors sum up their results in the following lines.

"The alkaline halids colored by the cathode rays show an alkaline reaction; their essential physical and chemical properties are *identical* with those of the substances obtained chemically by treating with a metal of the alkalies. From the method of preparation these latter contain *subchlorids* (or dissolved metal according to Elster and Geitel) and we must therefore assume the same for the first mentioned substances." *W. D. B.*

On the permeability of some liquids for heat rays of great wave-length. *H. Rubens and E. Aschkinass. Wied. Ann.* **64,** *602 (1898).* — The order of permeability in 5 mm layers is benzene, carbon bisulfid, xylene, phenol, and ethyl alcohol, benzene being the most permeable substance that has yet been investigated. *W. D. B.*

On absolute determinations of heat radiation with the electric compensation pyrheliometer, with examples of the application of this instrument. *Knut Angström. Wied. Ann.* **67,** *633 (1899).* — The author offers the present description and application pyrheliometer in consideration of the fact that as yet only preliminary notes have been published. The principle of the method is very simple and, as the author shows, is capable of considerable accuracy with simple electrical measuring instruments. Two blackened platinum surfaces are used, one of which is subjected to the influence of the radiating body, and the other is screened and heated by an electric current. When the temperature of the two strips is the same, determined by a thermocouple attached to the back side of the strips, then the electrical energy used in warming the protected strip gives a measure of the heat received by the other strip. The strips are made reversible and are also both exposed to the radiating source for adjustment to equality. Examples are given showing the method of determining the constants of the instrument, and an extensive series on the strength of solar radiation made simultaneously with two instruments, one at Guimar, 360 m above sea-level, and one at "Alta Vista," 3252 m above the sea. The author proposes the use of the Hefner lamp as a standard of radiation. *H. T. B.*

On the charge of electricity carried by the ions produced by Röntgen rays. *J. J. Thomson. Phil. Mag.* [*5*] **46,** *528 (1898).* — "The theory of the method used is as follows: By measuring the current passing through a gas exposed to Röntgen rays and acted upon by a known electromotive force, we determine the value of the product nev, where n is the number of ions in unit volume of the gas, e the charge on an ion, and s the mean velocity of the positive and negative ions under the electromotive force to which they are exposed.

The value for v was taken from Rutherford's data, while n was determined by measuring the size of the drops in a cloud caused by an expansion of dust-free air or hydrogen while exposed to the Röntgen rays. The value of e in air is calculated to be 7.3×10^{-10} electrostatic units; in hydrogen the uncorrected value is 6.7×10^{-10}. A correction for nuclei formed independently of the rays would probably make this latter value the same as that in air. These values are of the same order as the charge carried by the hydrogen ion in electrolysis.

W. D. B.

On the law of spectral series. *T. N. Thiele. Astrophys. Jour.* **6,** *65 (1897).* — A discussion of the consequences of the assumption that the law which expresses the wave-lengh λ of the lines of a series as a function of the series number n of the lines must have the form $\lambda = f[(n+c)^2]$, where c is a constant. *W. D. B.*

Investigation of the violet part of some metallic spectra which contain many lines. *O. Lohse. Astrophys. Jour.* **6,** *95 (1897).* — The metals studied were cerium, lanthanum, didymium, thorium, yttrium, zirconium, vanadium, and uranium. *W. D. B.*

Changes in the wave-frequencies in the lines of emission spectra of elements, their dependence upon the elements themselves, and upon the physical conditions under which they are produced. *W. J. Humphreys. Astrophys. Jour.* **6,** *169 (1897).* — A further study (see **1,** 332) of the effect of pressure on wave-lengths. The following conclusions are formulated:

1. Increase of pressure causes all isolated lines to shift towards the red end of the spectrum.

2. This shift is directly proportional to the increase of pressure.

3. It does not depend upon the partial pressure of the gas or vapor producing the lines, but upon the total pressure.

4. The shift of the lines seems to be nearly or quite independent of temperature.

5. The lines of bands (at least of certain "cyanogen" and aluminum oxid bands) are not appreciably shifted.

6. The shifts of similar lines of a given element are proportional to the wave-lengths of the lines themselves.

7. Different series of lines (as described by Kayser and Runge) of a given element are shifted to different extents. When reduced to the same wave-length these shifts are to each other approximately as 1 : 2 : 4, respectively, for principal, first and second subordinate series.

8. Similar lines of an element, though not belonging to a recognized series, are shifted equally (when reduced to the same wave-length), but to a different extent than are those unlike them.

9. Shifts of similar lines of different substances are to each other, in most cases, inversely as the absolute temperatures of the melting-points of the elements that produce them.

10. The shifts of similar lines of different substances are to each other approximately as the products of the coefficients of linear expansion and cube roots of the atomic volumes of the respective elements (in the solid state) to which they are due.

11. Analogous or similar lines of elements belonging to the same half of a Mendelejeff group shift proportionally to the cube roots of their respective atomic weights.

12. The lines of those substances which, in the solid form, have the greatest

coefficients of linear expansion have the greatest shifts. The converse is also true.

13. The shift of similar lines is a periodic function of atomic weight, and consequently may be compared with any other property of the elements which itself is a periodic function of their atomic weights. *W. D. B.*

The new series in the spectrum of hydrogen. *J. R. Rydberg. Astrophys. Jour.* **6,** *233* (*1897*).—Reasons are given for believing that the two series of hydrogen are to be represented by two distinct formulas. *W. D. B.*

On triplets with constant differences in the line spectrum of copper. *J. R. Rydberg. Astrophys. Jour.* **6,** *239* (*1898*).—Two groups of triplets have been found. Hitherto triplets have been recognized only in the spectra of biatomic elements, and the series of copper was supposed to be made up of doublets. *W. D. B.*

On the constitution of the red spectrum of argon. *J. R. Rydberg. Astrophys. Jour.* **6,** *338* (*1897*).—The conclusion is reached that "the red spectrum of argon belongs to one single element." *W. D. B.*

Crystallography, Capillarity, and Viscosity

On the spreading out of liquids and phenomena connected with it. *J. Stark. Wied. Ann.* **65,** *287* (*1898*).—A discussion of surface-tension phenomena with special reference to two-component systems. Owing to the change in surface-tension due to change of temperature, soot will rise in chloroform exposed to direct sunlight, and will sink if the chloroform be shaded. *W. D. B.*

On the measurement of coefficients of viscosity. *P. A. Guye and L. Friderich. Bull. Soc. Chim.* (*3*) **19,** *164* (*1898*).—Measurements show that Ostwald's method of measuring coefficients of viscosity is nearly as accurate as that used by Thorpe and Rodger. *W. D. B.*

On the theory of capillary electrical phenomena. *E. Warburg. Verh. phys. Ges. Berlin,* **17,** *24* (*1898*).—A discussion of the difference between the theories of Helmholtz and of Warburg. Helmholtz assumes that the entire polarization current is used to change the thickness of a double layer, while Warburg assumes that only a small portion of the polarization current is utilized in forming a double layer, the remainder being spent in electrolysis. For the same electromotive force between mercury and an electrolyte the two theories call for a double layer of the same strength, but of very unequal thicknesses, the thickness being enormously greater according to the Helmholtz theory than according to the Warburg theory. *W. D. B.*

On the relations between the surface-tension of some amalgams in electrolytes and the electrocapillary phenomena. *G. Meyer. Verh. phys. Ges. Berlin,* **17,** *47* (*1898*).—The capillary constant a of mercury polarized in sulfuric acid to a maximum surface-tension is 42.1 mg/mm. The capillary constant for tin amalgam, 0.0796 pct Sn, is 37.5; for cadmium amalgam, 0.48 pct Cd, is 38.2; of zinc amalgam, 0.059 pct Zn, is 36.9. The capillary constant of sodium amalgam in sodium sulfate solution is less than that of mercury in the same solution. *W. D. B.*

ON THERMAL AND DYNAMIC COEFFICIENTS

BY J. E. TREVOR

On page 523 of the present volume of this Journal, I presented a calculation of the forms which the thermal and dynamic coefficients of isotropic one-phase systems of constant mass and composition assume when they are expressed as functions of the partial derivatives of each of the four fundamental thermodynamic functions **E**, **F**, **G**, **H**. It was there noticed that the results, as regards their form, arrange themselves in a striking manner in three groups. The question arises why this is so.

A closer examination of the matter makes clear that the end actually sought was a series of expressions for all the possible partial derivatives,

$$\left(\frac{\partial \eta}{\partial p}\right)_v \quad \left(\frac{\partial \eta}{\partial p}\right)_\theta \quad \left(\frac{\partial \eta}{\partial \theta}\right)_p \quad \left(\frac{\partial \eta}{\partial \theta}\right)_v \quad \left(\frac{\partial \eta}{\partial v}\right)_p \quad \left(\frac{\partial \eta}{\partial v}\right)_\theta$$

$$\left(\frac{\partial v}{\partial p}\right)_\theta \quad \left(\frac{\partial v}{\partial p}\right)_\eta \quad \left(\frac{\partial v}{\partial \theta}\right)_p \quad \left(\frac{\partial v}{\partial \theta}\right)_\eta \quad \left(\frac{\partial v}{\partial \eta}\right)_p \quad \left(\frac{\partial v}{\partial \eta}\right)_\theta,$$

of the entropy and of the volume. (It should not be overlooked that the last two derivatives in either row are the reciprocals of the last two in the other.) Looking at the matter in this way, it becomes obvious that in the most general form of the problem we are required to find all the twelve mutual ratios of the differentials of the quantities, p, v, θ, η, which appear in the energy equation

$$d\mathbf{E} = -pdv + \theta d\eta.$$

When we do so, it will be seen at once that the results fall naturally into three groups of four each.

In the problem as set, the quantities p, v, θ, η in the initial differential equation are connected by two independent relations, say

$$f(p, v, \theta) = 0$$
$$\phi(\eta, v, \theta) = 0,$$

so that any two are functions of the other two. We are to find the twelve mutual ratios of dp, dv, $d\theta$, $d\eta$, in terms of the derivatives of the function $\mathbf{E}$. The problem falls naturally into two parts, in one of which the extensities v and η, in the other the intensities p and θ, are successively maintained constant. In its development in general form I am indebted to my colleague, Professor James McMahon, for very helpful suggestions.

In the first of these parts we set out with

$$\begin{cases} -p = \dfrac{\partial \mathbf{E}}{\partial v} \\ \theta = \dfrac{\partial \mathbf{E}}{\partial \eta}; \end{cases}$$

whence

$$\begin{cases} -\left(\dfrac{\partial p}{\partial \eta}\right)_v = \dfrac{\partial^2 \mathbf{E}}{\partial v \partial \eta} & (1) \\ -\left(\dfrac{\partial p}{\partial v}\right)_\eta = \dfrac{\partial^2 \mathbf{E}}{\partial v^2} & (2) \end{cases}$$

$$\begin{cases} \left(\dfrac{\partial \theta}{\partial \eta}\right)_v = \dfrac{\partial^2 \mathbf{E}}{\partial \eta^2} & (3) \\ \left(\dfrac{\partial \theta}{\partial v}\right)_\eta = \dfrac{\partial^2 \mathbf{E}}{\partial \eta \partial v}; & (4) \end{cases}$$

and, further, by division,

$$-\left(\frac{\partial p}{\partial \theta}\right)_v = \frac{\dfrac{\partial^2 \mathbf{E}}{\partial v \partial \eta}}{\dfrac{\partial^2 \mathbf{E}}{\partial \eta^2}} \qquad (5)$$

$$-\left(\frac{\partial p}{\partial \theta}\right)_\eta = \frac{\dfrac{\partial^2 \mathbf{E}}{\partial v^2}}{\dfrac{\partial^2 \mathbf{E}}{\partial \eta \partial v}}. \qquad (6)$$

In attacking the second part of the problem, we set out from

$$\begin{cases} dp = \dfrac{\partial p}{\partial v}\,dv + \dfrac{\partial p}{\partial \eta}\,d\eta \\ d\theta = \dfrac{\partial \theta}{\partial v}\,dv + \dfrac{\partial \theta}{\partial \eta}\,d\eta. \end{cases}$$

For constant p (i. e. for $dp = 0$) we have, rewriting the first of these equations, and eliminating dv (or $d\eta$) between both,

$$\frac{dv}{-\dfrac{\partial p}{\partial \eta}} = \frac{d\eta}{\dfrac{\partial p}{\partial v}} = \frac{d\theta}{\begin{vmatrix} \dfrac{\partial p}{\partial v} & \dfrac{\partial p}{\partial \eta} \\ \dfrac{\partial \theta}{\partial v} & \dfrac{\partial \theta}{\partial \eta} \end{vmatrix}};$$

or

$$\frac{dv}{\dfrac{\partial^2 \mathbf{E}}{\partial v \partial \eta}} = \frac{d\eta}{-\dfrac{\partial^2 \mathbf{E}}{\partial v^2}} = \frac{d\theta}{-\mathrm{H}_e};$$

writing H_e for the Hessian of $\mathbf{E}$. From this double equation follow, successively,

$$-\left(\frac{\partial v}{\partial \eta}\right)_p = \frac{\dfrac{\partial^2 \mathbf{E}}{\partial v \partial \eta}}{\dfrac{\partial^2 \mathbf{E}}{\partial v^2}} \tag{7}$$

$$-\left(\frac{\partial v}{\partial \theta}\right)_p = \frac{\dfrac{\partial^2 \mathbf{E}}{\partial v \partial \eta}}{\mathrm{H}_e} \tag{8}$$

$$\left(\frac{\partial \eta}{\partial \theta}\right)_p = \frac{\dfrac{\partial^2 \mathbf{E}}{\partial v^2}}{\mathrm{H}_e}. \tag{9}$$

Taking θ constant, we find, in the same way,

$$-\left(\frac{\partial \eta}{\partial v}\right)_\theta = \frac{\dfrac{\partial^2 \mathbf{E}}{\partial v \partial \eta}}{\dfrac{\partial^2 \mathbf{E}}{\partial \eta^2}} \tag{10}$$

$$\left(\frac{\partial \eta}{\partial p}\right)_\theta = \frac{\dfrac{\partial^2 \mathbf{E}}{\partial v \partial \eta}}{\mathbf{H}_e} \tag{11}$$

$$-\left(\frac{\partial v}{\partial p}\right)_\theta = \frac{\dfrac{\partial^2 \mathbf{E}}{\partial \eta^2}}{\mathbf{H}_e} . \tag{12}$$

The equations (1) to (12) furnish the desired expressions of all the ratios of the differentials dp, dv, $d\theta$, $d\eta$. They show it to be a necessary consequence of the initial equation and the two attendant conditions, that these expressions should fall, as regards their form, into the three groups:

GROUP I. SECOND DERIVATIVES

Equations	(1)	(2)	(3)	(4)

GROUP II. RATIOS OF SECOND DERIVATIVES

Equations	(5)	(6)	(7)	(10)

GROUP III. RATIOS OF SECOND DERIVATIVES TO THE HESSIAN

Equations	(8)	(9)	(11)	(12)

To obtain the corresponding expression of these twelve partial derivatives, in terms of the second derivatives of each of the other fundamental functions **F**, **G**, **H**, we merely require, in each case, to treat the corresponding initial differential equation in exactly the manner employed above. With the equations (1) to (12) before us, the desired results can be found by inspection.

Cornell University, September, 1899

THE ELECTROLYTIC REDUCTION OF POTASSIUM CHLORATE

BY ADOLPH L. VOEGE

With the exception of some papers dealing with organic compounds,[1] very little has been published on quantitative electrolytic reduction,[2] and there is in consequence no satisfactory theory of the subject. The object of the work to be described in this paper was to gather data which might serve before long as a basis for a complete theory of electrolytic reduction. While the experiments have not been carried far enough to warrant theoretical deductions, a number of interesting facts have been observed, all of which will have to be accounted for at some future time. It was deemed best to study the reduction of an inorganic compound because the theory of electrolytic dissociation could be applied to the results. From an experimental point of view two things were essential. The compound must be one that is not readily reduced, so that there may be a possibility of the total yield varying very much with changing conditions, and either the original compound or the reduction product must be one that can be determined analytically with ease. Both requisites are satisfied in potassium chlorate, and this salt was therefore taken as the substance to be studied. The conditions affecting this reduction are but little known. In this research the most important points investigated were: the presence of

[1] Elbs, Jour. prakt. Chem. (2) **43**, 39 (1891); Binz, Zeit. Elektrochemie, **5**, 5 103 (1898). Cf. also Elbs, Zeit. Elektrochemie, **2**, 472 (1896); **4**, 87 (1897); **4**. 499 (1898); Elbs and Kopp, Ibid **5**, 108 (1898); Elbs and Schwartz, Ibid **5**, 113 (1898); Löb, Ber. chem. Ges. Berlin, **29**, 1894 (1896); Zeit. Elektrochemie, **2**, 532 (1896); **3**, 471 (1897); **4**, 428 (1898); Rohde, Ibid. **5**, 322 (1899); Haber, Ibid. **4**, 506 (1898).

[2] The work of Freer and Higley, Am. Chem. Jour. **21**, 377 (1899,) had not been published when this research was begun.

acid and alkali; the use of different metals as cathode; the current density; the concentration of the acid; the temperature of the electrolyte; the presence in solution of a salt of the electrode metal. The first point to be determined was the relative reduction in acid and alkaline solutions, all other conditions being the same. Oettel's method of following a reaction by measuring the gas evolved was adopted, though the amount of chlorid in the acid solutions was afterwards checked by titration with silver nitrate. Two cells, one containing acid and the other alkali, were arranged in series with a sulfuric acid voltameter, a copper voltameter and an ammeter, this last instrument being placed in circuit to facilitate keeping the current constant. A little electric motor run by a storage cell was used to keep the solution in the copper voltameter well stirred. The current for electrolysis was obtained from the dynamo circuit, and regulated in amount by tapping from a resistance frame until the desired drop in voltage was obtained. The loss of weight at the anode of the copper voltameter was always found to be greater than the gain in weight at the cathode. The solution was made up according to Oettel's formula and it was found that the discrepancy was due to the free acid which dissolved copper from both anode and cathode, making the loss of the former too great and the gain of the latter too small. This conclusion followed from a run in which the electrodes were placed in the electrolyte, and all the conditions remained exactly as in the previous runs, except that no current passed. It was found that the loss from both electrodes, after a period of time equal to that of the previous runs, very nearly accounted for the discrepancy just mentioned. To use this correction would necessitate keeping the strength of the acid in the electrolyte and the immersed surface of the electrodes always the same. These conditions were difficult to satisfy and a constant correction is therefore nearly impossible. It was thought more accurate to take the mean value of gain and loss, for the loss from the anode is $x + a$, when x is the loss due to electrolysis and a is the loss due to free acid, and the gain at the cathode is $x - a$. If the mean of these values be taken, a is

eliminated and the true value of x is obtained from which the current must be computed. This method introduces a chance for error if the anode contains impurities, for these may fall from the electrode or be dissolved by the acid at a different rate. Nevertheless, this method has been followed throughout this research, and in every run the copper voltameter has been used to determine the current flowing.

The burettes were calibrated with mercury and the correction due to the difference of level between the water inside and outside the burette was determined experimentally, using hydrogen. In the first series of experiments, the electrolyte in one cell consisted of 120 cc of half-normal potassium hydroxid solution and 120 cc of potassium chlorate solution saturated at about 16°; in the other cell was 120 cc of quarter-normal aqueous sulfuric acid and 120 cc of potassium chlorate solution. Amalgamated zinc was used as anode and platinum foil as cathode. That the gas might be collected, the cathode was placed under an inverted cylindrical glass funnel from which a tube ran to the collecting burette. The wire leading to the cathode was sealed into a glass tube. Distilled water was used in the gas burettes to avoid the possibility of the hydrogen reacting with any impurity that might be present.

In this series of experiments the current strength varied from 0.04 to 0.67 ampere, the area of the cathode was about 6 cm², while the temperature of the inner solution was kept at 25°. The duration of the runs was generally two hours, and

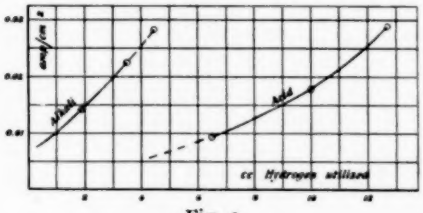

Fig. 1

every ten minutes readings were taken of the current, the oxygen and hydrogen evolved in the voltameter, and the hydrogen

evolved at the cathode of the acid and the alkaline cells. The utilization of hydrogen in the acid and the alkaline cells at different current densities, is shown in Fig. 1, the ordinates being amp/cm² and the abscissas cubic centimeters of hydrogen. The circle at the upper end of the alkali curve should be at the lower end of the same curve.

The values of hydrogen utilized are the differences between the hydrogen evolved in the sulfuric acid voltameter uncorrected and that evolved in the burettes. These curves show that, with the current densities employed, at least three times as much reduction occurs in the acid as in the alkaline solutions. Since the increase in the hydrogen utilized for a given increase of current density becomes less and less as the current density increases, and since the total amount of hydrogen generated increases at the same rate as the current density, it follows that the percentage reduction decreases with increasing current density. In other words, the efficiency of electrolytic hydrogen is greater with a low current density than with a high one.

The trend of the curve for the acid cell seems to lead to the origin, which means that no hydrogen is utilized when no current passes, while the curve for the alkaline cell reaches its zero of hydrogen utilization while there is still considerable current flowing. This inclines one to the opinion that there is some constituent of the cell important as a reducing factor, the electromotive force of polarization of which has not been reached under the conditions of the run until a current flowed sufficient to cause current density of 0.0065 amp/cm².

The amount of hydrogen that should be evolved during any run, as calculated from the average current derived from the copper voltameter, was found to be always actually less than that given off in the oxy-hydrogen voltameter. In the first run, for instance, there are 620 cc of hydrogen evolved in the voltameter. Assuming 0.03738 gram of hydrogen generated per ampere hour, in two hours with a current of 0.672 ampere, 0.0502 gram of hydrogen would be given off. At 0° C there are 0.08987 gram of hydrogen per liter or one gram per 11.127 liters.

The increase in the volume of hydrogen per degree centigrade is 0.00366, and as the temperature of the room during the run was about 22°, the increase in volume over that at 0° C is 0.08; therefore a gram's volume at room temperature is 12.02 liters, or a liter of hydrogen weighs 0.0831 g. During the run of two hours, therefore, $\frac{0.0502}{0.0831} \times 1000 = 606$ cc of hydrogen should be evolved. This discrepancy between 620 and 606 cc is probably due to the mechanical transfer in the voltameter of the oxygen liberated at the anode by the current to the cathode tube. With a strong current this phenomenon can be distinctly observed. This is substantiated by the disagreement observed in the hydrogen and oxygen volumes at any instant in the voltameter, for the volume of hydrogen is always more than twice that of the oxygen generated. This last is not conclusive, however, as ozone is formed to some extent at the anode, and being triatomic it reduces the volume of the oxygen of which it is formed by one-third. Peroxide of hydrogen, H_2O_2, may also be formed, thereby taking oxygen in solution, and would also tend to increase the variation between the observed values in the manner stated. The quantities of hydrogen evolved as observed and those calculated from the current strength were plotted, and it was then seen that these curves were both straight lines, so that the mechanical transfer of oxygen or whatever other action produces the disagreement is a function of the current, i. e. the voltage alone.

A quantitative test for the reduction in the foregoing runs was made by analyzing all the solutions for chlorid. The method first employed was by titration with silver nitrate, and ammonium sulfocyanate, both $n/10$ and exactly equivalent, using ferric ammonium sulfate as indicator. Several difficulties were encountered with this method. The titration must be rapid as the indicator fades quickly. It was also noticed that the excess of silver nitrate added seemed to change the end-point, though this end-point was at no time clearly marked. So titration was abandoned and another method resorted to. This was to add a quantity of the silver nitrate solution to the solution to be

analyzed, to allow the solution to clear and add silver nitrate again, continuing this process until one drop of silver nitrate produced no cloud in a solution which has cleared completely. This method proved much more satisfactory and several portions of the same solution analyzed for a check agreed exactly whenever tried. The disadvantage of this operation is the time it takes. This inconvenience was overcome to a considerable degree by heating the solution during the analysis to about 75° C and also by shaking the precipitate violently when formed. This last was accomplished by employing a machine transforming rotational into reciprocating motion. By turning a crank, a bottle containing the solution and precipitate, and firmly attached to the reciprocating portion, was shaken violently up and down. By using three burettes as many solutions could be analyzed at the same time, and time is saved which would otherwise be lost in waiting for the precipitate to settle after shaking.

On analysis, by the first method here, very small quantities of chlorid were found, though traces were observed in all solutions, outer and inner. This was to be expected, as the maximum quantity of hydrogen utilized, 12 cc, corresponds to 0.001 gram, which means the formation of about 0.013 gram of potassium chlorid. This is much larger than the analysis showed, in this instance 0.003 gram, which would seem to indicate that four-fifths of the reduction here was in the formation of potassium hypochlorite, and as a matter of fact this latter salt, detected by the odor, was always present to some extent.

In all cases, the inner solution was clouded by the nitrate solution more than the outer, but in no case did the efficiency of the yield, i. e. the ratio of hydrogen utilized to the total hydrogen evolved, rise above six percent.

From this series of runs it is evident that hydrogen electrolytically evolved has little tendency at ordinary temperatures to reduce potassium chlorate.

TABLE I

Alkaline cell

Amp	Cathode Amp/cm²	Average Temp	Hydrogen evolved Voltam	Calc	Cell
0.672	0.105	30°	620.	593.5	634.0
0.147	0.023	21	140.	133.0	138.0
0.089	0.014	19	84.	79.3	83.3
0.046	0.007	19	44.1	40.9	44.3
			Acid cell		
0.672	0.084	29°	620.	593.5	617.5
0.147	0.029	21	140.	133.0	124.0
0.089	0.018	18	84.	79.3	72.3
0.046	0.009	18	44.1	40.9	36.9

In Table I are given the principal data obtained from four runs of the above series. From these data it is seen that the hydrogen evolved from the acid solution is always less than that from the alkaline, the latter being always nearly the same as that given off in the voltameter. If we assume that this last quantity is correct, notwithstanding the disagreement between it and the volume of oxygen evolved, then a slight reduction does occur in the alkaline cell as shown by the smaller quantity of hydrogen evolved therefrom. If, however, we assume the value of hydrogen generated in the voltameter to be erroneous, and that the value calculated from the current determined by the copper voltameter is correct, then in the alkaline solutions no reduction takes place, but on the other hand some chemical action occurs by which hydrogen is liberated independent of electrolysis. Unfortunately, the reduction in the alkaline solutions could not be quantitatively determined, as it was discovered after the runs were made that the potassium hydroxid used contained chlorid, and as the quantity of reduction at the most was very small, it was deemed inadvisable with the limited time at our disposal to repeat the experiments with purer alkali.

A series of experiments was next made investigating the effect of the metal used as cathode, and the effect of current density upon the reduction. These experiments were of much

promise, as Thorpe[1] had found that the reduction of ferric sulfate by direct action of a metal was possible, and that this reduction was greater with zinc than with magnesium, equivalent weights of the metal dissolved being considered. However, the time in which a reacting weight of magnesium is dissolved is much less than for the equivalent quantity of zinc. Franchot[2] eliminated this effect and found that the difference still existed, and that electrolysis caused as much reduction of ferric salts at the anode as at the cathode, whence he concluded that metals such as zinc, cadmium, and copper reduce the salt directly, though indirect reduction due to the action of the acid on the metal also occurred. Franchot further states that from some experiments he has made upon the reduction of potassium chlorate, it is probable that the above-named metals act directly upon the salt to reduce it.

Gladstone and Tribe[3] found a similar reaction in the direct reduction of potassium nitrate by zinc, care being taken by using pure amalgamated zinc to prevent galvanic action. Later, however, they reject the explanation of the direct action of the zinc.

Johnson[4] states, however, that finely divided copper does not reduce potassium chlorate. He did not try the effect of adding acid.

Neumann[5] states that all metals act directly upon solutions of their nitrates.

The conclusion to be drawn from these papers is that if for the platinum cathodes zinc or cadmium cathodes are substituted the reduction will be greater, due to the direct action of the metal upon the chlorate. This reaction can be written as follows:

$$3Zn + KClO_3 + 3H_2O = KCl + 3Zn(OH)_2.$$

[1] Jour. Chem. Soc. **41**, 287 (1882).
[2] Jour. Phys. Chem. **1**, 75 (1896).
[3] Jour. Chem. Soc. **33**, 144 (1878).
[4] Jour. Chem. Soc. **35**, 240 (1879).
[5] Zeit. phys. Chem. **14**, 193 (1894).

As the solutions used are acid, the latter would break down, forming zinc sulfate. As potassium hydroxid is probably primarily formed at the cathode, due to the action of potassium as ion upon the water, potassium zincate may be formed :

$$Zn + 2KOH = Zn(OK)_2 + 2H.$$

This would cause more hydrogen to be evolved as shown, and the reduction consequently increased to a still greater degree.

In this series of experiments, cadmium and zinc were the metals chosen for consideration and were used in acid solutions only. The electrolyte in proportion and strength was throughout this set of experiments like that of the first series. The anode was in every case the same as the cathode in composition. The temperature was kept at about 65° C, its range of variation being about ten degrees. The temperature of the cells was kept nearly uniform by placing them upon sand baths. Thermometers were placed in the inner cells, the temperature observed every five minutes and the average of these readings is presented. A Weston ammeter was placed in the circuit to observe and regulate the current during the run, the average current here and throughout all of the following runs being accurately obtained with the copper voltameter.

After the run, the inner solutions were diluted to 200 cc in a measuring flask, 50 cc of this drawn with a pipette and analyzed. This analysis in this series was always repeated two or three times as a check on the work.

TABLE II

No	Amp.	Amp/cm²	Average Temp	Percentage yield Cathode	Total
			Zinc cathode		
1	0.408	0.093	64.5°	26.0	27.2
2	0.420	0.058	64.3	33.4	36.2
3	0.413	0.027	64.3	50.0	51.2
4	0.378	0.019	65.1	58.2	59.1
			Cadmium cathode		
1	0.408	0.093	64.5°	26.8	27.6
2	0.420	0.058	64.7	30.9	31.0
3	0.413	0.029	62.5	31.1	31.3
4	0.378	0.015	62.0	31.1	31.2

The results of this series of four runs have been tabulated and are also shown graphically in Fig. 2.

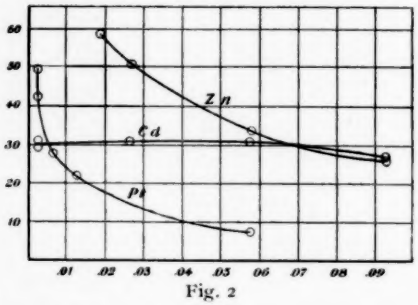

Fig. 2

From these results where the current and temperature have been kept practically the same, the great influence of current density at the zinc cathode is apparent. With the cadmium cathode this seems to have little or no effect and one must assume from this difference in behavior that the action of reduction in the zinc cell is different from that in the cadmium cell. This may be due to the formation of zincate for which there is no corresponding cadmium salt. As the surface of the zinc cathode was increased the zincate could more readily form, for then the KOH could react more quickly and before the sulfuric acid could change it to K_2SO_4.

It will be observed that the increase in yield increases at a rapid rate as the current density decreases. In attempting to follow this effect further, in order to increase the surface of the cathodes, the sticks of zinc and cadmium were replaced by hollow cylinders of the same metals. To obtain these, casting was found necessary. The patterns were made of low melting paraffin. They were formed by melting the paraffin in a beaker of hot water, on the surface of which it floats in a liquid layer. In this a glass cylinder, kept as cool as possible is plunged and immediately withdrawn, a film of the paraffin solidifying on its surface. This is repeated a number of times until the layer of paraffin is about 0.2 cm. in thickness. The paraffin is then cut,

longitudinally, stripped off, the cylinder greased with vaseline, the paraffin coating replaced, and the cut sealed by holding over a flame. The paraffin is now easily slipped from the glass and is then hardened.

An attempt was first made to pour the castings in plaster of Paris; but though the plaster was heated for about twelve hours at a temperature of 100° C, too much moisture was still present and the metal on pouring was blown from the mould. Castings can be made in this way, but the plaster must be heated until almost all of the moisture is driven from it, just enough remaining to prevent crumbling. This requires careful attention, and the method was abandoned and the castings were poured in sand, first melting the paraffin forms out.

Several runs were made with the two cylinders thus obtained under the same conditions as in the last series, and it was found that although the yield with the cadmium remained about constant, that with the zinc was very greatly reduced. These data are given in Table III.

TABLE III

No	Amp	Amp/cm²	Average Temp	Cathode yield
		Zinc cathode		
1	0.431	0.0035	64.4°	15.9 pct
2	0.445	0.0036	64.0	24.0
3	0.417	0.0034	63.4	36.9
4	0.406	0.0122	65.1	39.6
5	0.425	0.0034	60.0	42.1
6	0.406	0.0033	64.6	47.0
		Cadmium cathode		
1	0.431	0.0037	65.4°	31.7 pct
2	0.445	0.0038	65.5	31.0
3	0.417	0.0036	63.6	29.9

Extrapolating on the curve for the variation of the percentage yield with respect to current density (Fig. 2), an efficiency of 75 or 80 percent was expected from the Zn cell. On the first run, 16 percent was obtained; repeating under the same conditions, this efficiency rose to 24 percent; from a third run 37 per-

cent was obtained, and the fourth gave 47 percent. From a fifth run at 60° instead of 65° with a slightly higher current density, both tending to decrease yield, 42 percent was obtained. From these results it is evident that casting had some effect on the outer surface of the Zn, which gradually wore away.

Though cast in dry sand which had been baked to melt the paraffin, the surface was probably chilled to some extent and resisted much more the action of the acid, due to the formation of smaller crystals in the metal. From the chip broken off of the cylinder after the fifth run, this formation of small crystals near the surface and larger ones within was still noticeable.

To test this effect more thoroughly two sticks of zinc were cut in two pieces; one piece of each stick laid aside, and the other piece cast in the same form. One of the pieces was cast in cold moist sand in order to harden; the other in a hollow brass cylinder which was first cut longitudinally and then the two halves joined and wrapped with asbestos and wire and heated. The former method, however, was found to produce a much harder casting than the latter. This could scarcely be due to any action of the brass in forming an alloy, as, in pouring, the zinc had welded with the brass, and, on removing the brass, a layer of zinc adhered to its surface. Had an alloy been formed, the tendency would have been to soften the casting. The results obtained were probably due to the different temperatures of the zinc when poured.

A photograph, showing the effect of the different conditions under which the electrodes were cast on the crystallization of the metal, was taken but is not reproduced in this article.[1]

Runs were made with these two cast pieces and the two uncast ones all used as cathodes and amalgamated, from which the following data were obtained:

TABLE IV

		Amp	Amp/cm²	Average Temp	Yield	Reduced yield
Uncast	II	0.4235	0.032	64.5°	72.3	75.6
Cast hard	I	0.4235	0.029	64.4	69.6	70.4
Uncast	IV	0.4035	0.028	66.3	65.3	65.3
Cast soft	III	0.4035	0.028	65.0	61.6	61.6

[1] Given in the author's thesis.

The data given here for "cast hard" are for the electrode cast in the brass cylinder. The corrections in the yield, for current density, were made from the zinc curve of Fig. 2, and the yields were all reduced to those for a current density of 0.028 amp/cm^2.

From these runs it will be seen that in each case from the uncast cathode a higher efficiency was obtained than from the cast, though the difference was not as marked as was expected from the action of the zinc cylinder. The difference in efficiency (corrected) between "hard cast" and uncast is greater than for the "soft cast" and its uncast portion, showing that the larger the crystals the better the yield. Why the efficiency for the uncast should be greater than for the "soft cast" is not under stood, as the crystals of the former are the finer. The age of the casting may, however, have something to do with this effect.

As in the second series of experiments the temperature had been raised, as well as substituting zinc and cadmium for platinum as cathode, it was thought advisable to make some determinations of the effect of temperature and current density with platinum again as cathode, to ascertain whether all the increased reduction obtained in the last series was due to the direct action of the metal or to increase in the temperature as well.

The following data resulted from these runs which were conducted in all respects like the previous set:

TABLE V

Amp	Amp/cm^2	Average Temp	Yield
0.4213	0.003	64.9°	49.0
0.4225	0.007	64.3	27.6
0.4225	0.013	65.3	22.1
0.4213	0.030	64.7	19.5
0.4213	0.058	64.0	7.6

These results are graphically shown in Fig. 2. Referring to this plate, it will be seen that although temperature and current density play important parts in raising the efficiency, some other factors enter into the zinc-cadmium series, for at the same

temperature and same current density the percentage yield with zinc or cadmium is three or four times that where the reduction is due to hydrogen alone, i. e. with platinum cathodes.

A series of determinations which proved fruitful in important results was next made to observe the effect of the concentration of sulfuric acid on the reduction. Six runs were made with temperatures, currents, and current densities practically alike. In these runs, the cathode solutions of $n/40$ and $n/20$ were alkaline at the end of the runs. The following table records the results obtained:

TABLE VI

Conc acid	Amp	Amp/cm²	Average Temp	Yield	Zn in solution
0.025	0.372	0.034	64.1°	3.0	0.894
0.050	0.372	0.034	64.1	6.9	0.879
0.225	0.389	0.034	64.9	34.3	0.902
0.250	0.389	0.034	65.2	61.5	0.925
0.500	0.376	0.034	64.4	84.2	0.958
1.250	0.376	0.034	64.3	77.4	0.886

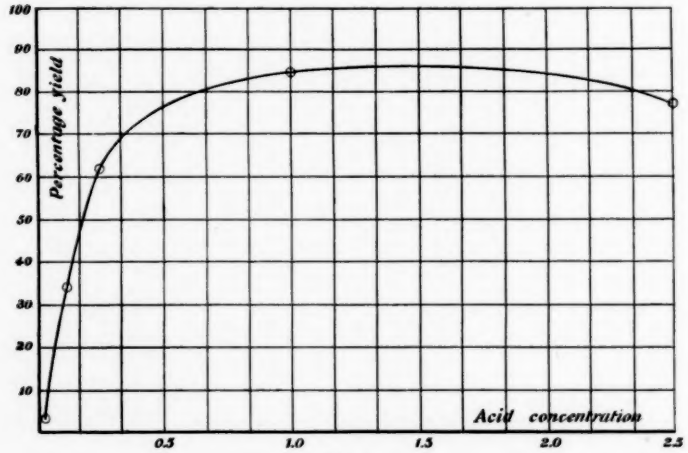

Fig. 3

From these results the reduction seems to be a function of the conductivity of the sulfuric acid. The percentage yield in-

creases greatly as shown, and, from the trend of the curve plotted, Fig. 3, seems to reach a maximum for acid of strength about three-halves normal. In the run with normal acid, the reduction in the outer cell was less than in any other run, though the cathode efficiency was the greatest. Sulfuric acid has a maximum conductivity at a concentration somewhat greater than four times normal, so something besides this conductivity must affect the result.[1] From this it would seem that the less the potassium chlorate carried the current the greater the resulting yield would be.

A series of runs was next undertaken to determine the effect of current strength on the reduction. The temperature was kept at about 65° C and the density at the cathode constant at 0.04 amp/cm². Three-halves-normal sulfuric acid was used; 120 cc of it and 120 cc of saturated potassium chlorate used per cell, as in all previous runs. The following results were obtained:

TABLE VII

Amp	Amp/cm²	Average Temp	Cathode yield	Total yield	Anode loss	Anode loss (calc)
0.063	0.050	64.2°	94.6	109.0	0.239	0.153
0.521	0.042	64.5	79.6	85.6	1.297	1.264
1.034	0.042	64.5	74.1	83.9	2.606	2.510
1.501	0.040	64.3	67.2	74.6	3.443	3.460
2.027	0.041	64.2	57.2	68.4	4.916	4.915

By inspection of the data it will be seen that the yield at the cathode appears to increase very distinctly with decreasing current; but that at the anode is a constant, meaning that at the anode the amount of reduction increases directly with the current strength, while at the cathode the reduction increases at a greater rate.

In this series, platinum wire was introduced into the solutions in an attempt to keep the zinc electrodes always covered and thereby keep the current density constant throughout the

[1] Since equal volumes of the sulfuric acid and potassium chlorate solutions are mixed, the actual volume concentration of the acid in the experiment is only about one-half that given in the table.

run, as otherwise, if only partially immersed, the portion of zinc in contact with the solution would change noticeably during a two-hour run, for an evaporation of from 12 to 15 cc occurs at a temperature of 65° C. The introduction of the platinum in the solution, however, produces a local action by which zinc is dissolved, hydrogen evolved (though not noticeably at the anode where this action should be the same as at the cathode), and the potassium chlorate is reduced.

The quantity of reduction due to this cause could be calculated knowing the anode loss, by computing the loss due to electrolysis for the current flowing, and to this adding the weight of zinc dissolved by the free acid in solution, at the temperature employed, and for given duration of run. The difference between this sum and the observed loss would give the loss due to the local action of the platinum.

Knowing this loss, the maximum reduction for which it can be held responsible can be calculated as follows:

For every two grams of hydrogen evolved 64.88 grams of zinc are dissolved; from the reaction $KClO_3 + 6H = KCl + 3H_2O$, for every 6 grams of hydrogen evolved 74.4 grams of KCl are formed, or for every 194.64 grams zinc dissolved 74.4 grams of KCl are formed, and therefore for every gram of zinc dissolved 0.3822 gram of KCl is formed.

As this is a constant independent of the strength of the current it will become a more important factor as the total reduction increases. That is, it will raise the apparent percentage yield, at the cathode, of the current of lower strength, as was found experimentally. If this is the case, however, the same effect should occur at the anode and the total percentage yield should increase at a greater rate than the percentage yield in the cathode cell. The data obtained certainly do not show this result.

Another proof that current does have an effect on the reduction is shown by comparing the efficiencies of runs for diffusion tests, and for zincate.[1] In the former test the current is

[1] See succeeding pages.

0.47 ampere, the cathode density 0.046, and the temperature 64° ; in the latter the current is 0.23 ampere, the cathode density 0.022 and the temperature 64°. The efficiency in the former case is at cathode 79.5, and in the latter 87.5 percent.

It seems probable, notwithstanding the annoying effect of the platinum, that increasing the current strength has the effect of decreasing the yield. This may be due to the change in voltage, which may cause some undesirable reaction, as possibly of the decomposition of $KClO_3$ or KCl, the former being undesirable as shown in experiments with varying strengths of sulfuric acid, the latter because it is the product desired.

The effect of increasing the temperature was next considered. Four runs were made at temperatures varying from 20° to 80°. In this series care was taken that the error due to the introduction of platinum did not enter, though the accuracy with which current density was determined suffered in consequence.

The following results were obtained :

TABLE VIII

Amp	Amp/cm²	Average Temp	Cathode yield	Total yield
0.436	0.042	25.6°	51.3	52.2
0.438	0.042	43.3	58.2	60.4
0.439	0.042	56.0	80.5	86.0
0.521	0.042	64.5	79.8	85.6
0.439	0.042	81.1	81.0	89.7

From the above data, it will be seen that the temperature is also an important factor. It is natural to expect results as here obtained, the efficiency increasing with increasing temperature, for increasing temperature always assists chemical action and thus less hydrogen escapes. Also, as seen from the anode reduction, it seems to increase the effect of the direct action of the zinc on the potassium chlorate. This anode reduction is not conclusive evidence as to the action of the zinc until an experiment has been performed, testing the amount of diffusion occurring from the cathode to the anode under the conditions of the run.

In all the runs made throughout this research some reduction is always found in the anode cell. This may be due to direct reduction by the zinc electrode or to diffusion from the cathode chamber. To settle this question, the anode and cathode were set in porous cups, each porous cup placed in a beaker, and the beakers connected by a siphon. The arms of the siphon had a diameter of about two centimeters so as to reduce the resistance as much as possible. As it was, the passage of the current sufficed to heat the liquid to about 70°. The electrolyte consisted of one part of $3n/2$ sulfuric acid and one part potassium chlorate solution.

A run of two hours was made with this apparatus, using 520 cc of the electrolyte, and heating the solutions in the beakers on sand baths to an average temperature of 64°. An average current of 0.4715 ampere was used, giving a current density at the cathode and anode of 0.046 ampere per square centimeter. The amounts of chlorid, determined by analysis, found in the cells were as follows, A referring to the anode and C to the cathode :

A inner (corrected)	0.002
A inner	0.004
A outer	0.005
C outer	0.031
C inner	0.347

It was determined and will be explained at length further on, that zinc does reduce potassium chlorate in the presence of sulfuric acid; and due consideration being paid to the effect of temperature, length of run and area of metal exposed to the electrolyte, the correction was applied to "A inner" as shown above. From these results it will be seen that the reduction at the anode due to electrolysis is probably zero, and that in previous runs most of the chlorid found there came by diffusion from the cathode chamber, for the data show that the nearer the contents of the cell to the cathode the more the reduction found.

To determine the amount of reduction due to the hydrogen evolved from the purely chemical action of the sulfuric acid on

the zinc, a stick of amalgamated zinc having an area of 10.3 cm^2 was immersed in 120 cc. of the standard solution of potassium chlorate and sulfuric acid ($3n/2$) at a temperature of about 70° C for two hours. The loss of zinc was 0.0145 g, and on analysis of the solution 0.0015 g of potassium chlorid was found.

It had seemed probable from the results previously obtained that under the proper conditions an electrolytic efficiency of more than 100 percent could be obtained at the cathode. This would mean that hydrogen was evolved from something other than direct electrolytic action. If the potassium chlorate carries the current, the K ions will appear at the cathode and decompose water, forming KOH and H. From Faraday's law this H would be part of that calculated from the current strength together with that due to the transference of H ions from the H_2SO_4. The KOH formed would ordinarily react with the acid, forming water and K_2SO_4; but if this acid were eventually weakened at the cathode, the alkali might act upon the zinc and form the zincate with evolution of hydrogen, as follows:

$$Zn + 2KOH = Zn(OK)_2 + 2H.$$

This H is not accounted for by the electrolytic calculation and is a purely secondary reaction, so, should it react with the chlorate, at a low current density, an efficiency better than unity is quite possible.

To determine whether this reaction occurs, the hydrogen evolved from the cathode was measured, and this quantity added to that used in reduction, determined by analysis, should equal the total evolution calculated from the current strength, if no zincate is formed. If the zincate is formed the sum of the above quantities will be greater than the value calculated from the current.

The apparatus used in collecting the hydrogen has already been described, and special care was taken that the relative heights of the liquid columns remained the same, thereby preventing the necessity of recalibrating the burette. The cell was heated on a sand bath. The zinc cathode was suspended in an

inverted glass cylinder by platinum wires, care being used that the platinum did not come in contact with the electrolyte. This latter had the usual composition. An average current of 0.231 ampere was passed through the cell for two hours, the temperature averaging 64.3° C, and the current density 0.0225 amp/cm². 13.9 cc of hydrogen were evolved from the cathode during the run, and none from the anode, and on analyzing the solutions 0.1873 gram of potassium chlorid was found in the cathode cell and 0.023 gram in the anode cell.

At the temperature and pressure of the run 1 liter of hydrogen equals 0.08314 gram and therefore the 13.9 cc. of hydrogen evolved is equivalent to 0.00116 gram. The total potassium chlorid formed is 0.2103 gram, which corrected for the effect of the acid on the anode is 0.209 gram. This is equivalent to $\frac{0.209}{12.4} = 0.0169$ gram of hydrogen. The total hydrogen accounted for in the cell is therefore $0.0169 + 0.00116 = 0.0181$ gram; greater than that calculated from the current, 0.01727 gram, by 0.0008 gram or about 10 cc. An error which cannot be corrected for is the absorption of the hydrogen given off, by the water in the burette; this was undoubtedly less than 10 cc, and as hypochlorite was also detected in the solutions, thereby making the hydrogen accounted for still greater, the conclusion is reached that the zincate is formed and hydrogen evolved, through the action on the zinc of the potassium hydroxid formed electrolytically.

From the data obtained it should be possible to obtain a yield of over 100 percent, and to do this a run of two hours was made under the following conditions: 280 cc of the standard electrolyte was used, 100 cc of this in the cathode, the inner cell. The average temperature employed was 81° C, the current 0.0715 ampere, and the current density at the cathode 0.00134 amp/cm².

The anode lost 0.1984 gram in weight, the cathode lost 0.2760 gram in weight. On analyzing the solution 0.116 gram of potassium chlorid was found in the cathode cell and 0.0178

gram in the anode cell. From the current, 0.005335 gram of hydrogen should have been evolved, which, with an electrolytic efficiency of unity, would have formed 0.066 gram of potassium chlorid. The results from these data are an efficiency of 176 percent in the inner cell and a total efficiency of 202 percent. The reduction due to the presence of free acid is 0.0015 gram of potassium chlorid for an area of 10.26 cm^2 at a temperature of 65° C. Here at the cathode there is 5.2 times the area exposed, which would mean a reduction of $0.0015 \times 5.2 = 0.0078$ gram at the cathode, or as the temperature is in this case 15° higher, say 0.01 gram at the cathode and 0.002 gram at the anode where the area is 10.26 cm^2. If these quantities be subtracted from those already determined, the efficiencies are reduced to 160 and 184 percent.

No hydrogen was given off that could be observed, but from the following calculation it will be seen that hypochlorites must have been formed as the *electrolytic* efficiency of the *chlorid* yield is far from 100 percent. From the current strength the loss from the zinc anode should have been 0.1733 gram. It is actually 0.1984 gram. The difference, 0.0251 gram, is due to the action of the acid. Since 0.0251 gram of zinc is equivalent to 0.000773 gram of hydrogen, this means the formation of 0.00959 gram of potassium chlorid, assuming all the hydrogen to be used in reduction. If this be multiplied by 5.2, the ratio of the cathode to the anode area, the reduction due to the acid at the cathode, results, which is 0.0498 gram. Subtracting this from 0.106 gram gives 0.56 gram of potassium chlorid formed due to electrolysis or an electrolytic efficiency of 85 percent, while 15 percent of the hydrogen electrolytically evolved goes toward forming potassium hypochlorite. The loss in weight of the anode is probably wrong, as shown from this calculation. If the zincate is formed, a still greater quantity of hypochlorite may be formed, but it is hardly conceivable that this action can occur simultaneously with that due to the presence of the acid. A fact that tends to show that the zincate is formed, is shown in the data for the first series of experiments made,

Table I. In every case the hydrogen evolved from the alkaline cell is greater than that calculated from the current strength, showing that hydrogen is evolved from some chemical reaction other than those due to electrolysis. This reaction can be nothing else than the formation of potassium zincate.

Before undertaking any run with copper electrodes it was thought best to determine the reduction resulting from its presence in an acid solution.

120 cc of the standard electrolyte, sulfuric acid ($3n/2$) and potassium chlorate, was heated to about 70° C and a copper rod having an area of 11.5 cm^2 was immersed in the solution for two hours. No hydrogen was evolved, none gathered even on the metal; therefore all the copper dissolved was used to reduce the chlorate. 2.048 grams of copper were dissolved, and as one gram of copper is equivalent to $\frac{2}{63.18} = 0.0317$ gram of hydrogen, here 0.0649 gram of hydrogen was evolved which means the formation of 0.805 gram of potassium chlorid. On analyzing the solution 0.791 gram of potassium chlorid was determined, a yield of 98.2 percent of chlorid was obtained and 1.8 percent of the hydrogen must have gone to forming hypochlorite. It is interesting to note that under the same conditions, so far as they are known, zinc gave a yield of but 26 percent of chlorid and that therefore copper in the presence of sulfuric acid is a much better reducing agent than is zinc.

The dissolving of the copper is not due to the presence of the acid alone, for taking 60 cc of the acid ($3n/2$) and adding 60 cc of water, at the same temperature as the last run, with the same area of metal exposed, and in the same time but 0.0039 gram of copper was dissolved; while with the chlorate present 2.05 grams were dissolved.

Lastly, two runs of two hours each were made with copper electrodes at temperatures of 28° and 78°. In the former a current of 0.473 ampere flowed, the density at both the anode and the cathode being 0.049 amp/cm^2. During the run the anode solution became deep blue, the cathode remained colorless. The

loss in weight of the anode was 1.344 grams, while the loss of the cathode was 0.0036 gram. On analysis, at the anode, 0.0431 gram of potassium chlorid was found; at the cathode 0.0446 gram was found.

From the current 1.117 grams of copper should have been dissolved from the anode; as 1.344 grams were dissolved, 0.227 gram was due to the action of the acid. This quantity is equivalent to 0.0072 gram of hydrogen or 0.0893 gram of potassium chlorid. In the cathode cell the electrode lost 0.0036 gram, equivalent to 0.000114 gram of potassium chlorid. From the current, for an efficiency of unity, 0.4385 gram of potassium chlorid should be formed. Due to electrolysis, at the cathode, 0.0445 gram was formed, giving an efficiency of 10.1 percent; and at the anode, where 0.0893 gram was expected from the solution of copper besides some from diffusion, but 0.0431 gram was found. If the copper were absorbed as cuprous sulfate just half of 0.0893 or 0.0447 gram of potassium chlorid should be expected, which is much closer to the true quantity determined. These calculations reduce the electrolytic efficiency to 10.1 percent instead of 20 percent where all reduction is considered as due to electrolysis.

That electrolytically copper is less efficient than zinc may be shown by comparing this run with one of the runs for temperature determinations with zinc electrodes. In the latter run the current is 0.438 ampere, the density 0.042, and the temperature 26°, and the efficiency at the cathode 52 percent in a two hour run. The conditions are very closely those of the copper run and yet the electrolytic efficiency is five times as great in the run with zinc electrodes, notwithstanding that probably more than an equivalent weight of copper went into solution for the amount of zinc dissolved.

In the second run with copper electrodes a current of 0.0783 ampere was used, the density at both electrodes being 0.087 amp/cm^2. In this case the solutions were more deeply colored than in the previous run, that at the anode being much bluer than that at the cathode. The loss in weight of the anode is

2.64 grams and of the cathode 1.619 grams. On analysis, at the anode, 0.604 gram of potassium chlorid was found, and at the cathode, 0.878 gram. Here the anode loss due to the current is 0.185 gram, leaving the loss due to the acid and to the chlorate 2.455 grams, equivalent to 0.965 gram of potassium chlorid if we consider that the cupric compounds are formed. If cuprous compounds are formed 0.483 gram of potassium chlorid should be found; as 0.604 gram was found, the formation of both compounds may occur, or, the cuprous compounds being unstable, they may be broken down at the high temperature. The same explanation applies to the reaction at the cathode and no electrolytic efficiency can be at all accurately determined. It is, however, probably less than that with zinc electrodes.

The following conclusions are deduced from the results obtained experimentally:

1. The reduction occurring in acid solutions is greater than that occurring in alkaline ones.

2. The amount of reduction varies with the metal used for electrodes, being greater with the zinc than with cadmium and greater with the latter than with platinum.

3. With zinc and platinum the efficiency of reduction increases greatly with decreasing current density, while with cadmium this is not noticed.

4. The physical structure of the zinc electrodes greatly affects the reduction yield.

5. Increasing the temperature of the electrolyte greatly facilitates the reduction.

6. The reduction depends very largely on the strength of the sulfuric acid used. The efficiency being the maximum for acid of about three-halves normal strength.

7. Decreasing the current strength increases the reduction, this result being possibly due to the change in voltage occurring.

8. No electrolytic reduction occurs at the anode in zinc, cadmium, and platinum cells, and all chloride found there is due to the action of the acid and to diffusion from the cathode cell.

9. The potassium zincate is formed at the cathode by the secondary reaction of potassium hydroxide, electrolytically formed, with the zinc; and the hydrogen generated by this formation is used in reduction, making it possible to obtain an electrolytic efficiency of more than 100 percent.

10. Copper, though but slightly attacked by sulfuric acid alone, is readily dissolved in the presence of potassium chlorate, and an almost quantitative yield of potassium chlorid results.

11. This reduction by copper without electrolysis is about four times that by zinc for equivalent quantities dissolved, though zinc dissolves much more slowly than does copper.

12. With copper electrodes the electrolytic reduction is probably less than with zinc electrodes, though this is difficult to establish conclusively because of the great amount of reduction due to purely chemical causes occurring when copper electrodes are used.

The writer takes this opportunity to thank Professor Bancroft, under whose supervision this research was carried out, for the valuable advice he has always most willingly given. Thanks are also due to Mr. H. P. Cady, Fellow in Chemistry, for the many suggestions made by him with respect to the performance of experiments in the laboratory.

Cornell University, June, 1899

NOTE ON THE PREPARATION OF METALLIC LITHIUM[1]

BY LOUIS KAHLENBERG

Up to the present time metallic lithium has been obtained by electrolyzing lithium chloride in the molten state. The reason why this metal can not be obtained from aqueous solutions by electrolysis is that it reacts with water, forming hydrogen and lithium hydroxide. It is evident that if a solvent for a lithium salt could be found upon which lithium does not act, the metal could be deposited from the solution by electrolysis, provided the solution proved to be an electrolyte.

Pyridine is a solvent of this kind. It will dissolve lithium chloride and thus form a solution that conducts electricity. The electrical conductivity of such solutions is slight as compared with that of aqueous solutions. It has been determined by St. v. Laszczynski and St. v. Gorski.[2] These investigators also attempted to precipitate the metal from the solution electrolytically. In their electrolytic cell they used a diaphragm in form of a porous cup which greatly increased the internal resistance; and the cathode they employed was a short platinum wire 1 mm in diameter, so that the current density was relatively high. The anode consisted of a platinum foil. They used a pressure of 100 volts in their experiment in order to get a sufficient current. The result was that they obtained merely a black crust that contained metallic lithium.

I have found that lithium may be obtained in white metallic form from solutions of lithium chloride in pyridine by electrolysis at room temperatures. The method of operation is the sim-

[1] From the "Wisconsin Engineer," 3, 2 (1899).

[2] Zeit. Electrochemie, 4, 290 (1897).

plest possible. It may be described as follows: A concentrated solution of lithium chloride in pyridine is placed in a beaker into which dip a carbon plate (anode) and a bright iron plate or foil (cathode). Platinum or some other metal may, of course, also serve as cathode, though when used as anode a metal (even platinum) is apt to be attacked and some of its substance carried over to the cathode. No diaphragm is necessary. With a difference of potential of but 14 volts between the electrodes, a current of from 0.2 to 0.3 ampere per 100 sq. cm. of cathode area will soon deposit a dense, well-adhering silver white coating of metallic lithium. The deposit thus obtained possesses all the well known physical and chemical properties of the metal.

Lithium, being an alkali metal that is not very plentiful in nature, has thus far not found use in practical life in the metallic form; nor are the indications at present such that it will be used in practice. Metallic lithium costs from three to five dollars per gram and is used only for scientific purposes, mainly perhaps as a sample for exhibition in connection with lectures on chemistry.

By means of the method just described the metal can readily be obtained from the relatively cheap chloride in quantities sufficient for most scientific purposes. The method of preparation, as well as the properties of the metal, can thus easily be demonstrated to a class of students in a short time with simple means.

The method has not as yet been studied with a view of determining the conditions under which the yield is best, or to answer the question as to how large a quantity of the metal can thus be prepared economically. It may be stated, however, that the difficulties in obtaining lithium in quantity from this solution are in general those that are met in separating metals from their solutions in large quantities by means of the electric current.

Laboratory of Physical Chemistry, University of Wisconsin,
Madison, April 14, 1899

NEW BOOKS

Grundriss der allgemeinen Chemie. *By Wilhelm Ostwald. Third revised edition; 14 × 22 cm; pp. xvi + 549. Leipzig: Wilhelm Englemann, 1899. Price: paper, 16, cloth 17.20 marks.* — Though the same general form has been preserved, the third edition is very different from the first. There is less of the tentative and more of the dogmatic. The book is not now written to induce people to take up the study of physical chemistry, but to expound physical chemistry to them. A new point of view is manifest throughout. Not only is the physical chemist monarch of all he surveys; he has explored his new kingdom so thoroughly that there is little left to those who come after save to follow reverentially in the footsteps of the pioneers. There is a feeling of permanency that is impressive. Ostwald believes that all flesh is grass, except that of the physical chemist. While he preaches the doctrine that all theories spring up, flourish for a day, and then fade away, it is perfectly clear that physical chemistry is something different. Such matters as the change of the vapor-pressure with the concentration, as the potential difference between a metal and a solution, and many others, are no longer live questions. They have been settled for all time, and the only subject worthy the attention of a scientific man is that of catalytic action.

This may all be true. It sounds well, especially as Ostwald puts it, and yet one is sometimes tempted to ask whether we have not turned aside from the path along which true progress lies. When a student in Leipzig, nine years ago, I asked Ostwald whether it was not very desirable that some one should take up seriously the study of concentrated solutions. He thought not, saying that there was still too much to be worked out in regard to dilute solutions, and that it was well to finish that up before launching out into a new field. He believed that a further study of dilute solutions would make the question of the behavior of concentrated solutions an easy problem to solve. Nearly ten years have passed since then, and the science of physical chemistry has developed wonderfully during that time. But the matter of concentrated solutions is very nearly where it was ten years ago. The reason is not far to seek. Physical chemistry is not yet a quantitative science; it is a pseudo-quantitative science. There are all the outward signs of a quantitative science. We have formulas and tables; we make use of thermodynamics and the differential calculus; but this is for the most part a vain show. Long before we reach the point where the formula is to be tested experimentally, we slip in a 'simplifying assumption': that the concentration of one component may be considered as constant; that the heat of dilution is zero; that the solute may be treated in all cases as though it were an indifferent gas; that the concentration of the dissociated portion of a salt

may be substituted for the total concentration; etc., etc. The result is that our calculations apply at best only to limiting or ideal cases where an error in deducing the formula may be masked by the errors of observation. Helmholtz did not do this, but Helmholtz is considered old-fashioned.

The divisions of the book are: mass relations of chemical compounds; stoichiometry of gases, of liquids, and of solids; dilute solutions; general theory, including the periodic law and the molecular hypothesis; thermochemistry; chemical mechanics; photochemistry; electrochemistry; chemical affinity. As was to be expected, these last three chapters are the ones that are most unlike their forerunners in the first edition. There are, however, many changes throughout the volume. Among the satisfactory points are the general statement in regard to combining and formula weights; the table showing the experimentally determined vapor densities; the recommendation that the molecular rotation be referred to a layer one centimeter thick, the question of a negative surface-tension, and a standard unit of heat. This last is exceedingly interesting. Instead of the calorie, Ostwald proposes the kilojoule, $J = 10^{10}$ ergs. The relation of this to the 18° calorie, from Rowland's data, is 1 cal = 41830000 ergs, or $J = 239.1$ cal. There are now so many calories, and they are used so loosely and so indiscriminately, that the new unit is very welcome.

There are some points in the book that are distinctly not to be praised. In the deduction of Raoult's relation between vapor-pressure and concentration, there is absolutely nothing to show that the molecular weight of a solvent entering into the formula is the molecular weight of the solvent as vapor, and has nothing to do with the value in the liquid. The whirligig proof for the vapor given off by a dineric system is repeated, though without the cut. It is stated as a general truth that the higher-melting modification is always the more stable. The ohm is said to be equal to the resistance of a column of mercury 106.23 cm. long. Great pains are taken always to call the phase rule the phase law.

The book, as a whole, will prove serviceable to those wishing to get some idea of physical chemistry. The whole subject is given in a concise form, making the volume distinctly the best work that we have.

Wilder D. Bancroft

A Treatise on the Kinetic Theory of Gases. *By S. H. Burbury. 15 × 23 cm; pp. viii + 157. The Cambridge University Press. New York: The Macmillan Co., 1899. Price: $2.00.* — This is another treatise stimulated more or less directly by the sustained discussions published in Nature by Boltzmann, Burbury, Bryan, Watson, and others. The book before us is by no means elementary, in so far as it presupposes a sound knowledge of the subject. It is rather a critical examination of the kinetic theory of gases, beginning with carefully summarized definitions and hypotheses. The book is nowhere didactic; and it ends, as it were, with an appeal to the reader. Burbury distinguishes between the usual assumptions of the kinetic theory (Clausius, Tait, Boltzmann, and others), in which the chance of any molecule having a velocity, in the direction x, between u and $u + du$ is independent of its position in space, the velocities v, w in directions y and z, and the given instantaneous positions

and velocities of all other molecules of the system, — and a broader hypothesis in which these simplifying conditions do not hold. It is his purpose to assume the latter case, including as it does the first, and to show that the fundamental propositions can generally be established from the new point of departure. In Burbury's deductions, the distributing exponent of Maxwell's law, instead of containing squares of velocity only, becomes a quadratic function of these variables; and his propositions then apply to gaseous systems, without such restrictions as to density as limit the old kinetic theory. Throughout the book, the demonstrations are grouped around Boltzmann's minimum theorem, relative to the normal or persistent distribution of velocities in a gas.

The general reader will find the book interesting chiefly as an exhibit of the formidable difficulties which have hampered the progress of the kinetic theory of gases. *C. Barus.*

Physikalisches Praktikum, mit besonderer Berücksichtigung der physikalisch-chemischen Methoden. *By Eilhard Wiedemann and Hermann Ebert. Fourth, revised and enlarged, edition. 15 × 23 cm, pp. xxix + 574. Braunschweig: F. Vieweg und Sohn, 1899. Price: paper 10 marks, cloth 11 marks.* —The third edition of this work was reviewed two years ago (1, 734), and the fourth edition is now on the market. The general plan is the same as in the preceding editions. The additions are chiefly in the chapter on optics. We find a more complete discussion of photometers; experiments on the spherical and chromatic aberration of lenses, and on the determination of the focal distance in systems of lenses; new experiments on the application of spectrum analysis to analytical work; and what is practically a new chapter on the polarization of light. There are now two chapters instead of one devoted to conductivity measurements, and a similar expansion is to be observed in the pages relating to magnetic measurements. The book is very satisfactory and a large number of the experiments described therein should be performed by every student of chemistry. *Wilder D. Bancroft.*

The Fundamental Laws of Electrolytic Conduction. (*Harper's Scientific Memoirs.*) *Edited by H. M. Goodwin. 14 × 21 cm. pp. 8 + 98. New York: Harper and Brothers, 1899. cloth.* — There are reproduced in this volume two papers by Faraday, one the "Relation by Measure of Common and Voltaic Electricity," the other on "Electrochemical Decomposition;" one paper by Hittorf on the "Migration of Ions during Electrolysis;" and one paper by Kohlrausch on the "Conductivity of Electrolytes Dissolved in Water in Relation to the Migration of Their Components." The selection is a good one and the reviewer ventures the hope that a perusal of the two memoirs by Faraday will lead the student to study the "Experimental Researches" with care.
Wilder D. Bancroft.

Analyses électrolytiques. (*Encyclopédie scientifique des Aide-mémoire.*) *By Ad. Minet. 12 × 19 cm.; pp. 176. Paris: Gauthier-Villars, 1899. Price: boards 3 francs; paper 2.50 francs.* — This is another of the Aide-mémoire series. The book is distinctly above the average and contains directions both as to current and as to voltage. *Wilder D. Bancroft.*

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